

*Synchrotron Radiation and High Pressure: **NEW LIGHT AND NEW OPPORTUNITIES***

Russell J. Hemley

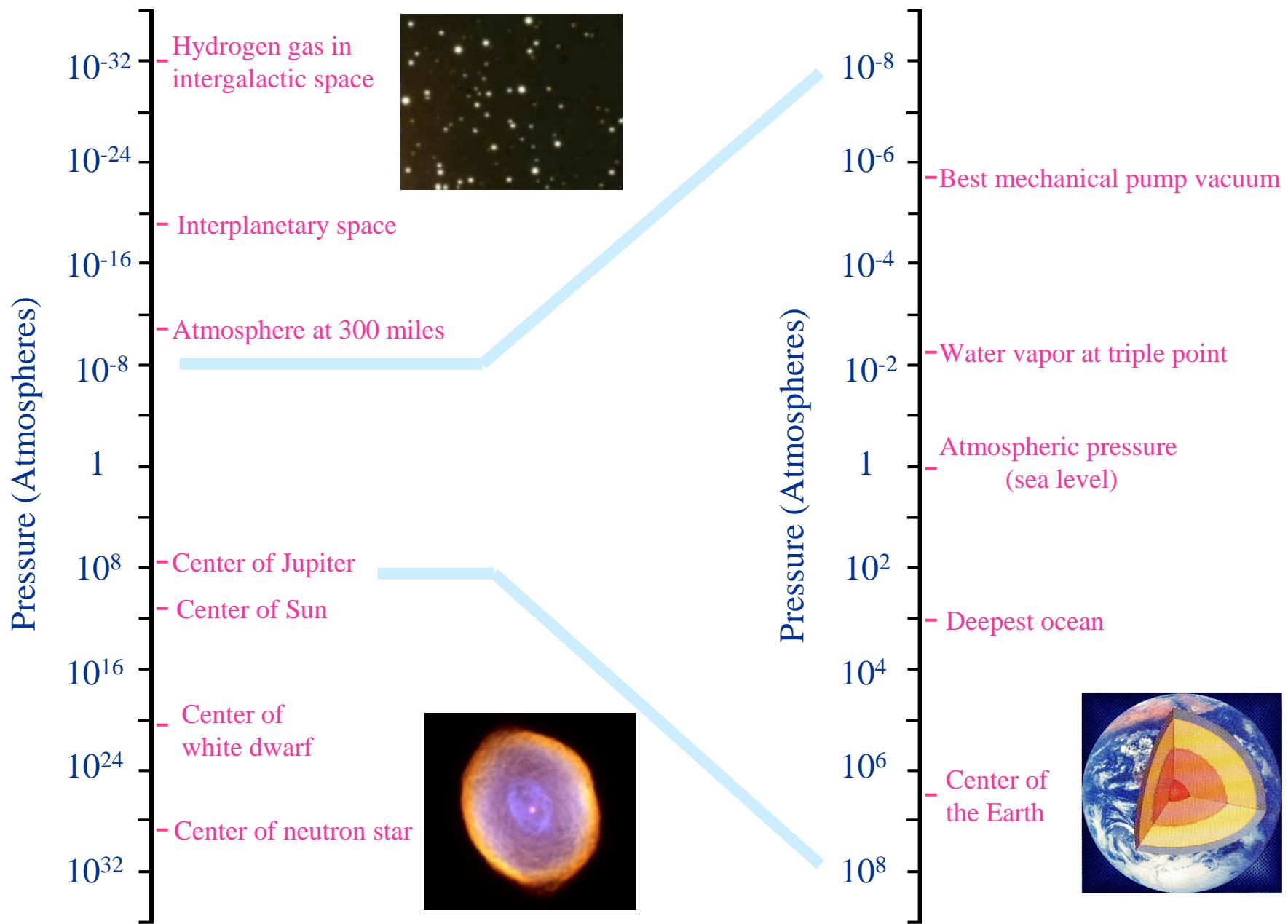


*Geophysical Laboratory
Carnegie Institution and CDAC*
Washington, DC*

* CARNEGIE/DOE ALLIANCE CENTER

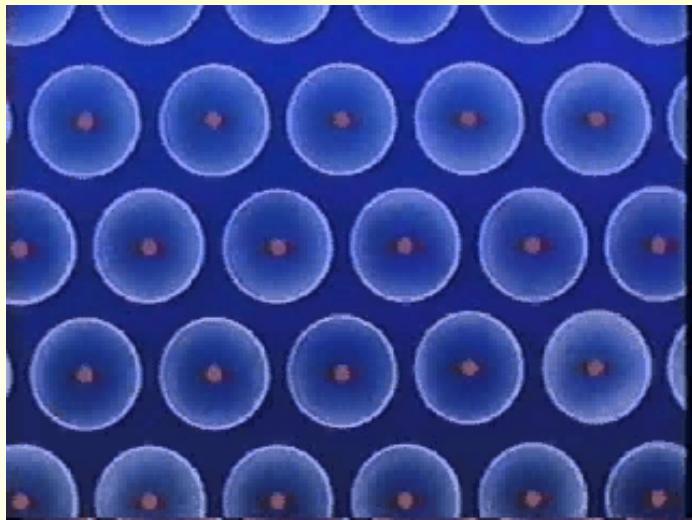


RANGE OF PRESSURE IN THE UNIVERSE

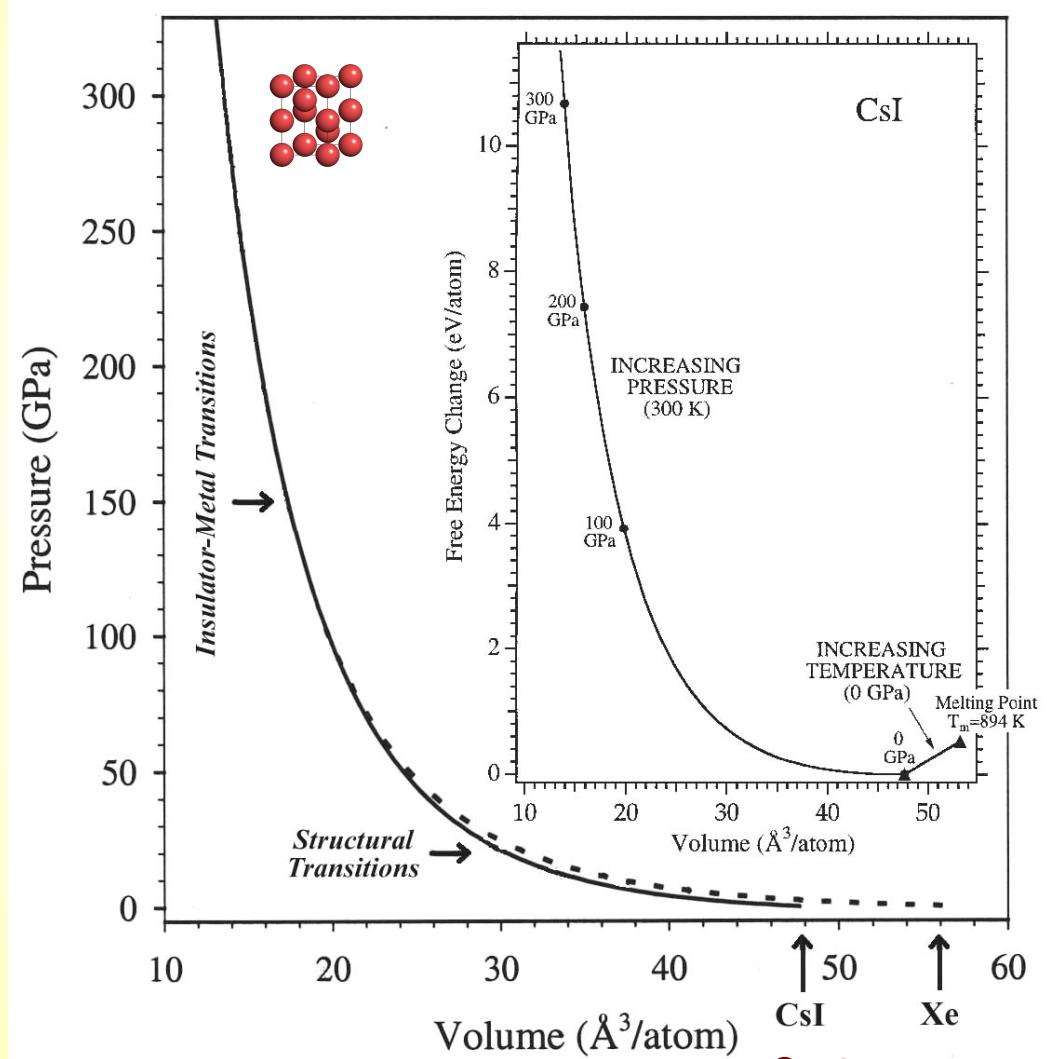
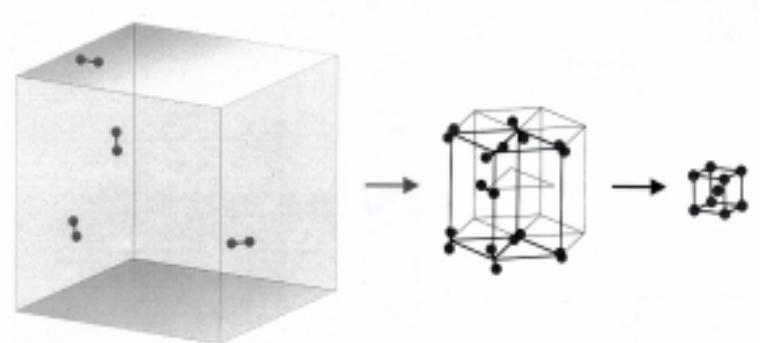


Chemical Bonding and Free Energies

Atoms

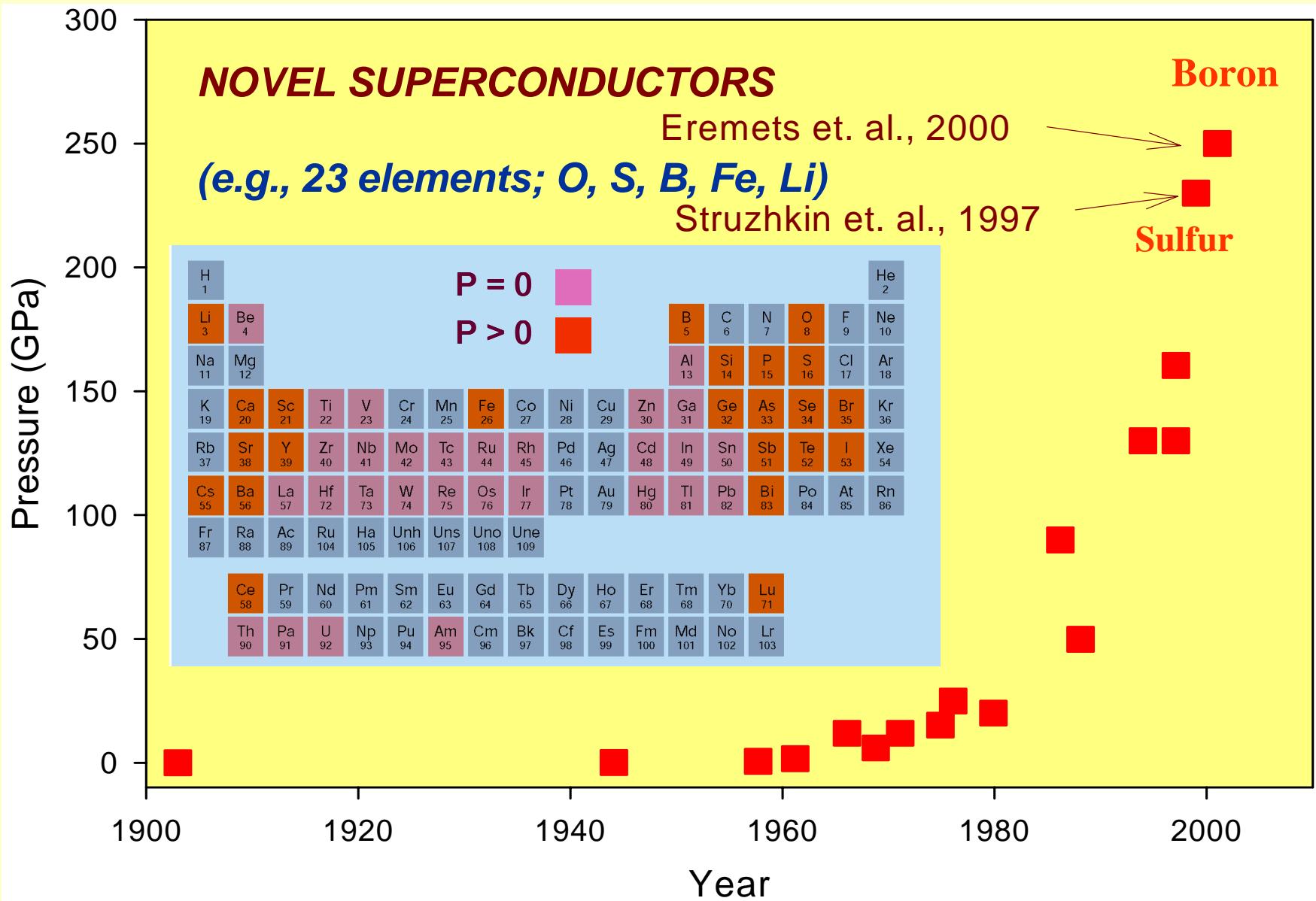


Molecules

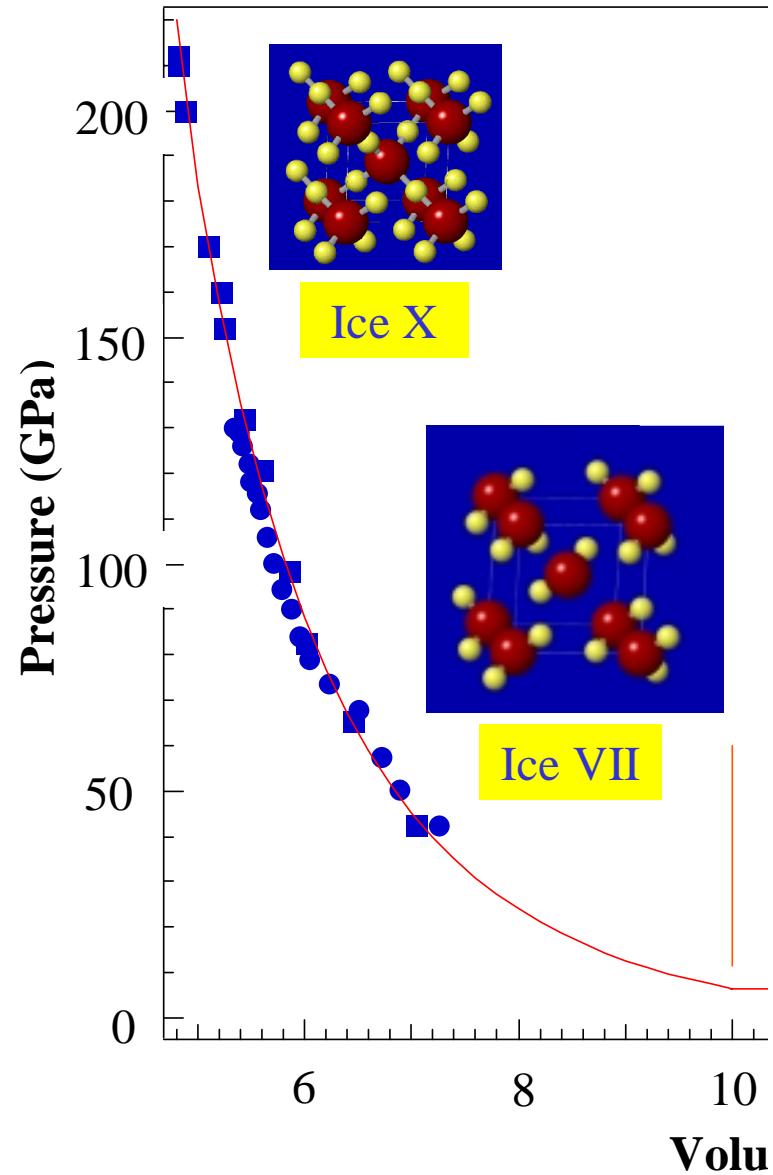


[Hemley and Ashcroft,
Physics Today 51, 26 (1998)]

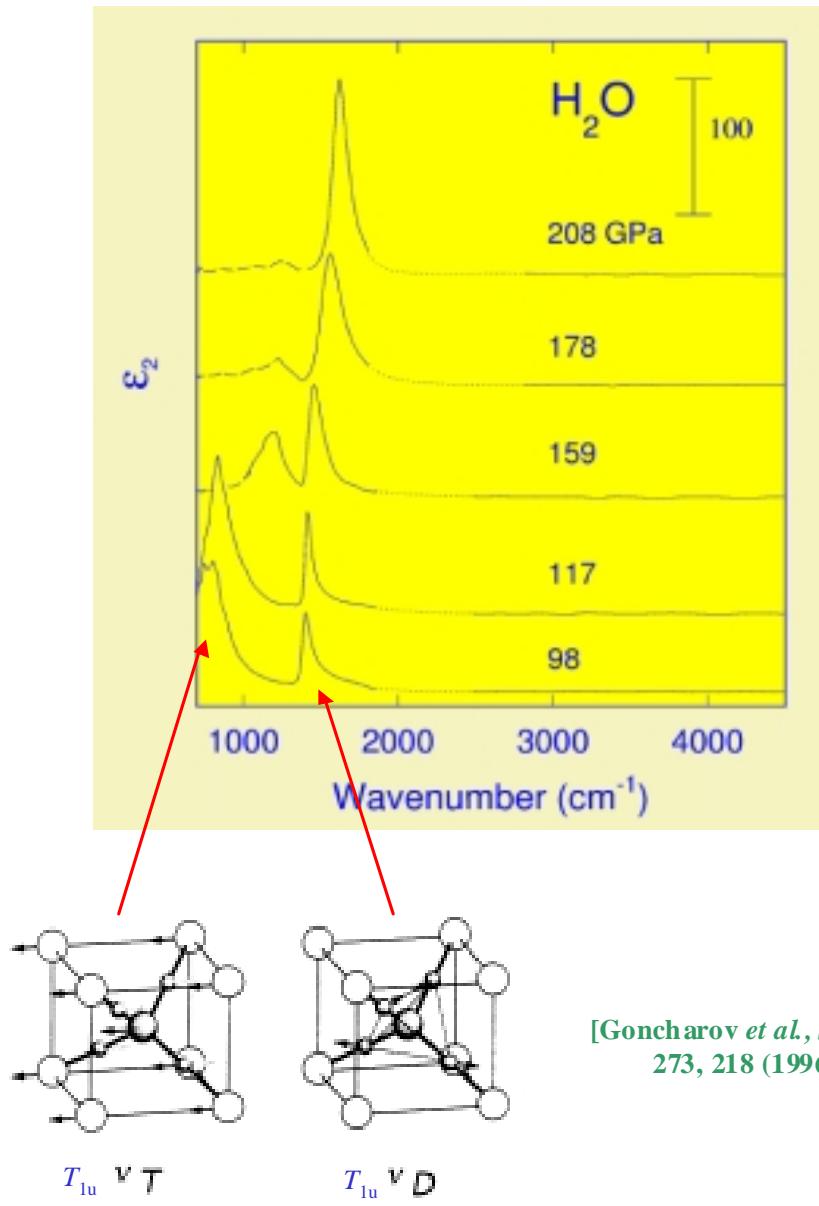
Prospects for superconductivity under pressure



Compression of H₂O



HIGH PRESSURE SPECTRA Synchrotron Infrared Reflectivity



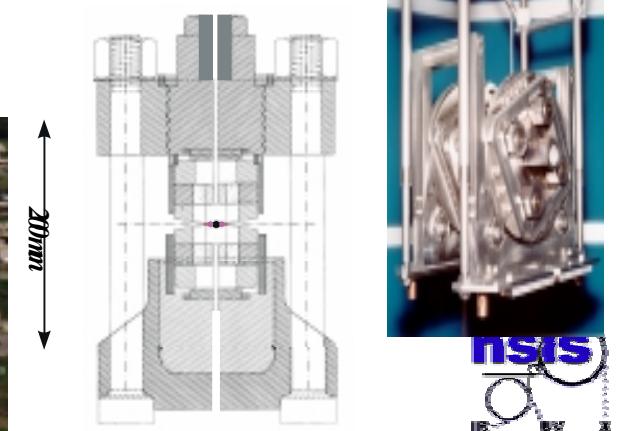
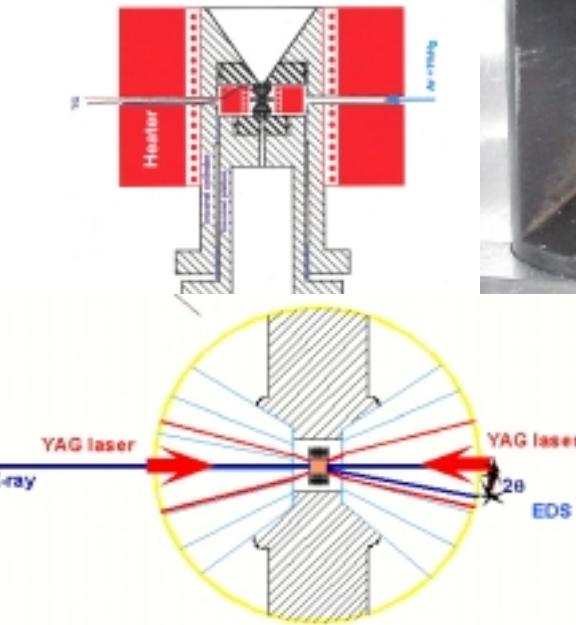
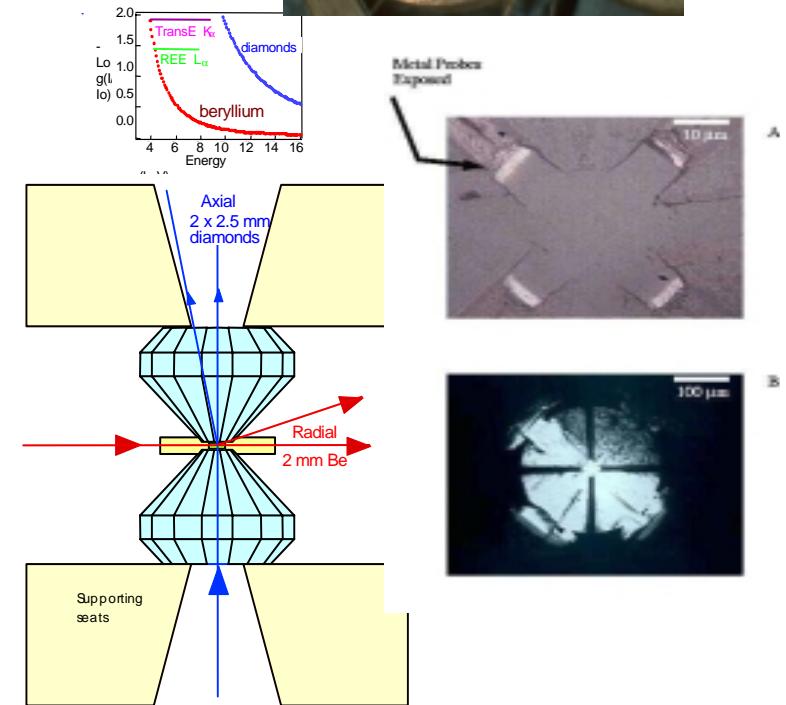
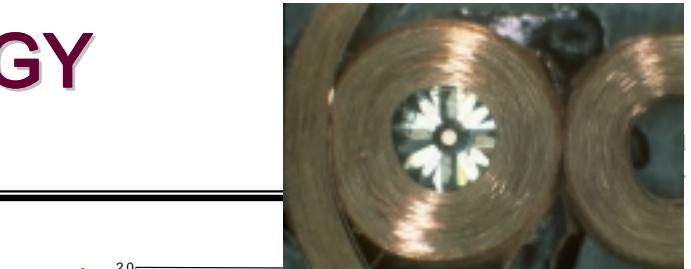
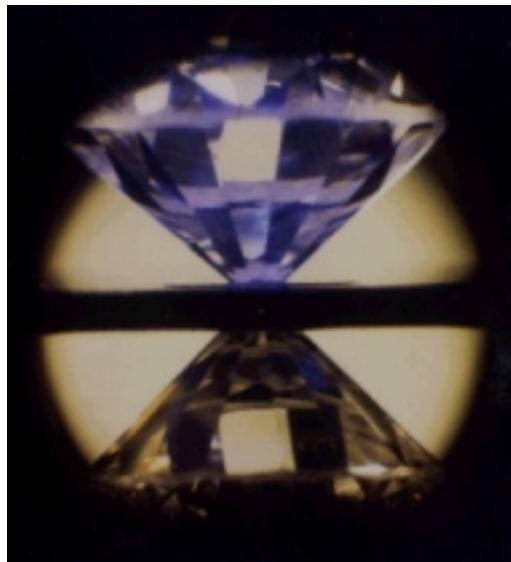
A Brave New World of Materials

- Novel transformations: solids, liquids, glasses
- Structures: unexpected complexity
- Molecules break down, but new ones form
- Novel electronic and magnetic phenomena
- New chemical reactions: low to high pressure
- New recoverable materials

- *Earth and Planetary Science*
- *Condensed Matter Physics*
- *Chemistry and Materials Science*
- *Biology and Soft Matter*

HIGH-PRESSURE TECHNOLOGY

Plethora of New Instruments



nsis

Numerous synchrotron techniques are now available for extreme conditions studies

Synchrotron Methods

Diffraction

- SINGLE CRYSTAL
- POLYCRYSTALLINE
- RADIAL
- SUB-MICRON

Spectroscopy

- K_B EMISSION
- EXAFS
- XANES

Inelastic Scattering

- PHONON
- ELECTRON
- NUCLEAR

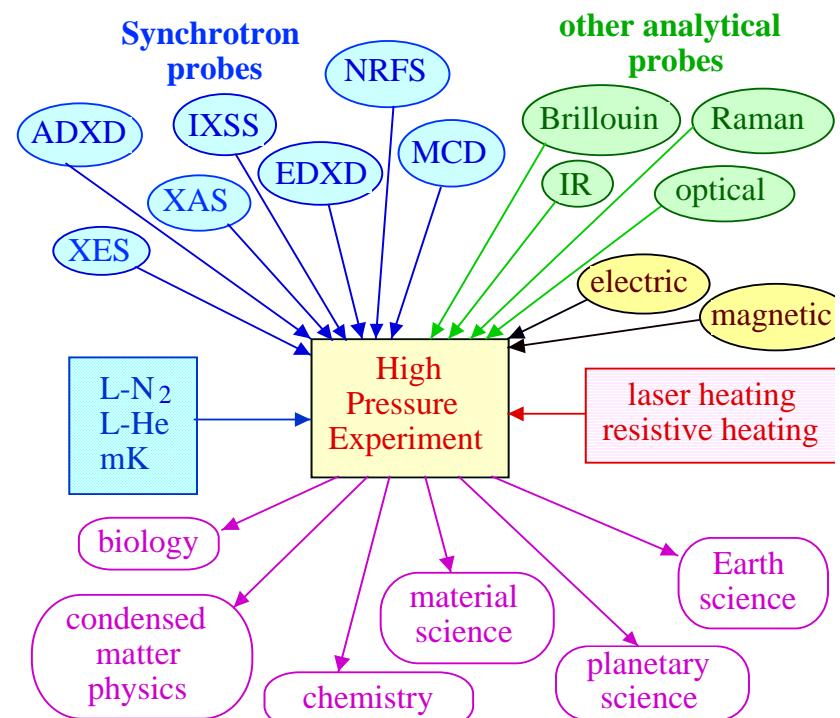
Radiography

- MICRO
- MACRO

Infrared Spectroscopy

- ABSORPTION
- REFLECTIVITY
- EMISSION

Integrated Probes

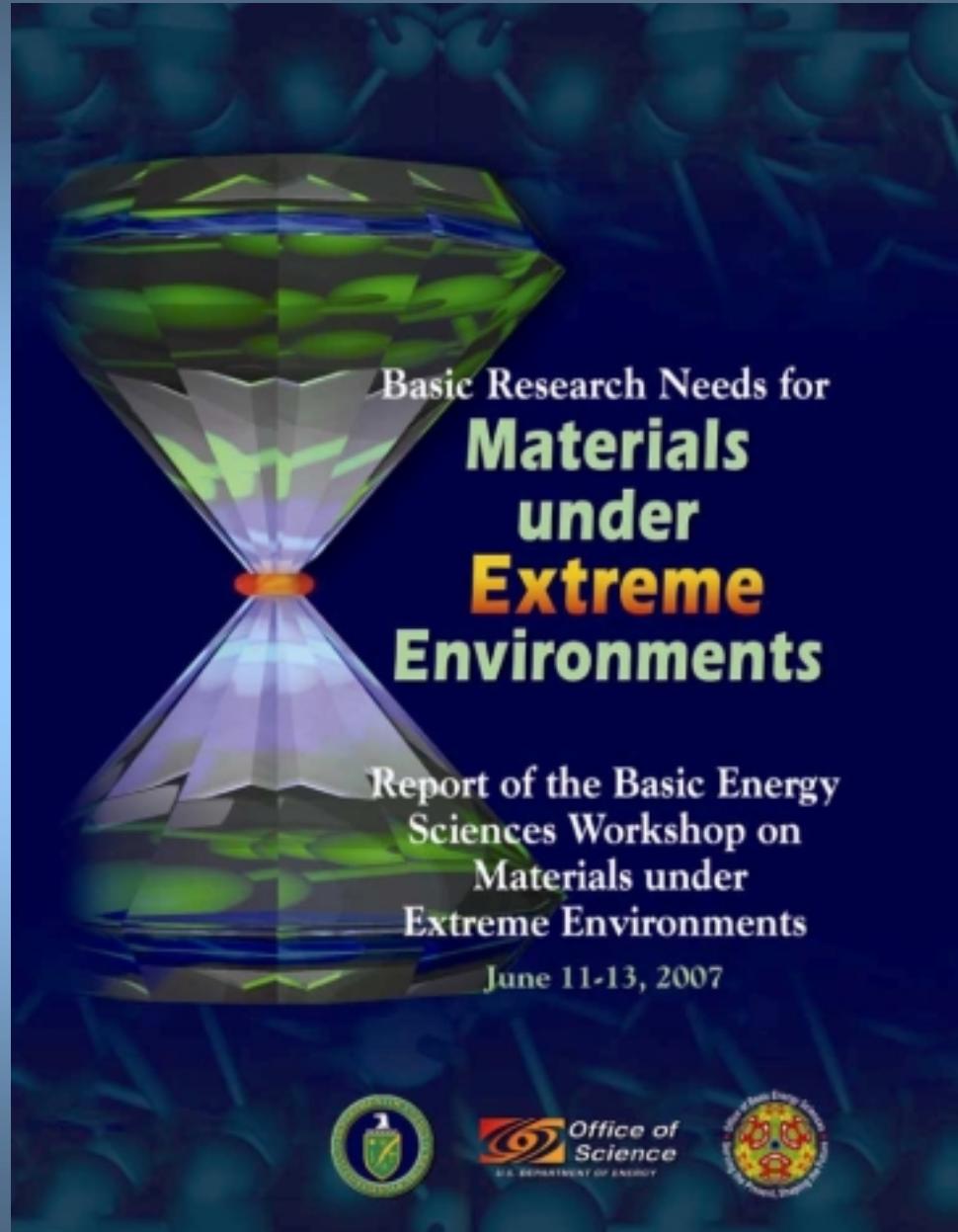


EXAMPLES

- 1. Hydrogen**
- 2. Novel Metals**
- 3. Dense Oxides**
- 4. New Techniques**
- 5. Conclusions**

THEMES

- *New phenomena*
- *Challenges for NSLS II*
- *Integration of techniques*
- *Broad implications*



Synchrotron radiation has been key to understanding dense hydrogen

1. HYDROGEN

DECEMBER, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME

On the Possibility of a Metallic Modification of Hydrogen

E. WIGNER AND H. B. HUNTINGTON, *Princeton University*

(Received October 14, 1935)

VOLUME 21, NUMBER 26

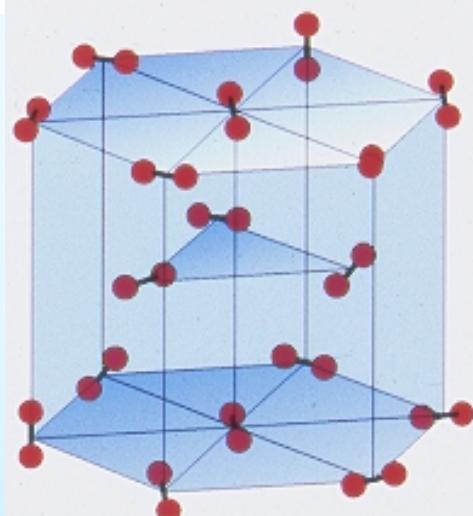
PHYSICAL REVIEW LETTERS

23 DECEMBER 1968

METALLIC HYDROGEN: A HIGH-TEMPERATURE SUPERCONDUCTOR?

N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 3 May 1968)



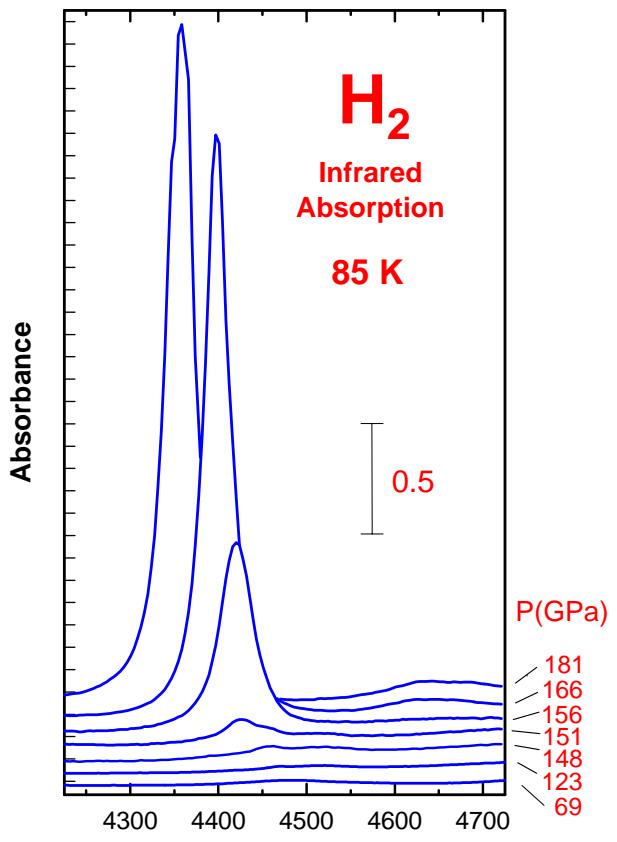
- Molecules stable to ~300 GPa in solid
- $\rho/\rho_0 \sim 14$ at 300 GPa

*First x-ray structure determination
dense hydrogen: hcp to >26.5 GPa*

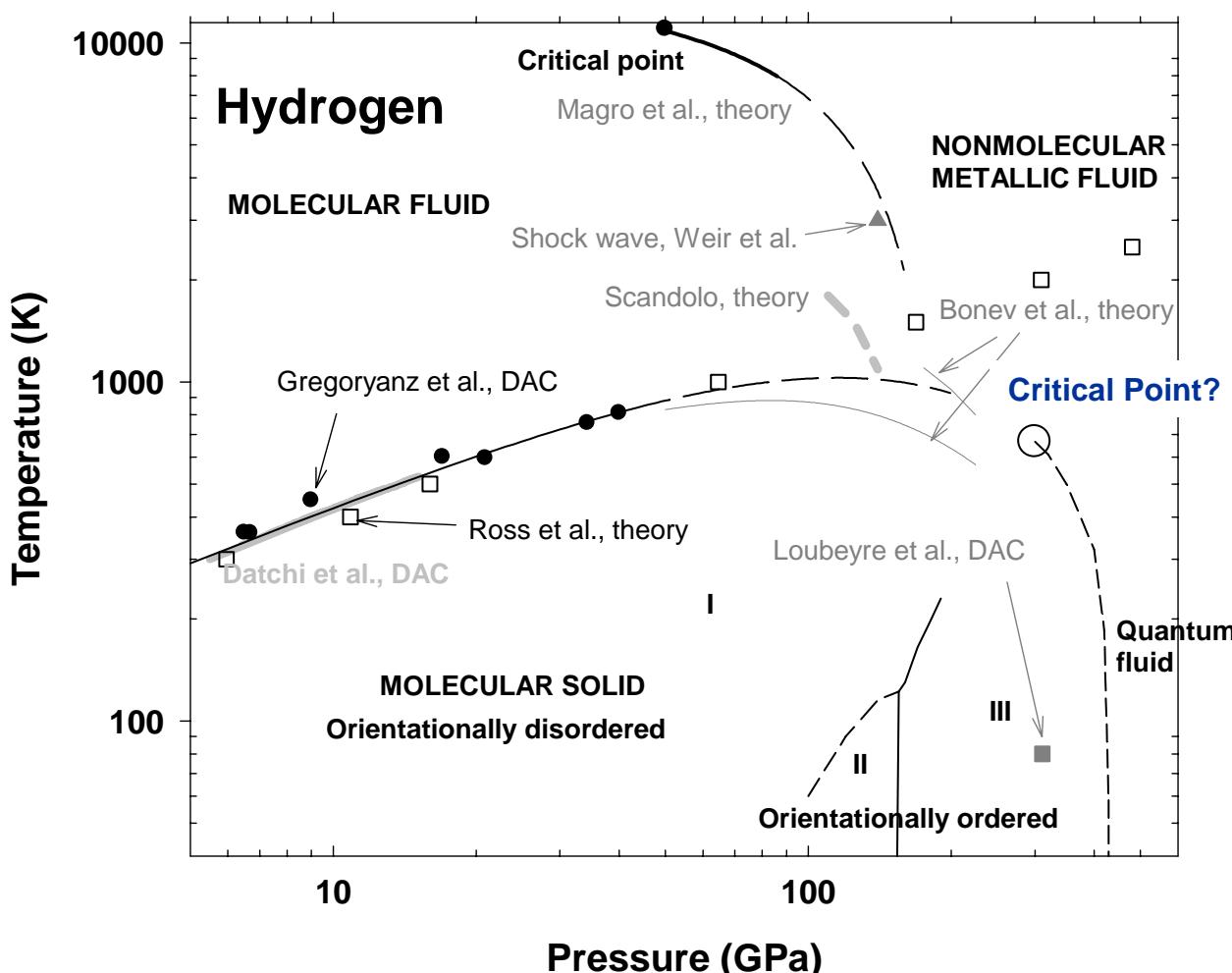
[Mao et al. *Science* (1988)]

“Ionic” charge-transfer state forms at 150 GPa; stable to >300 GPa

[Hemley et al. *Nature* (1994); Goncharov et al. *Proc. Nat. Acad. Sci.* (2002)]



Continuing puzzles of dense hydrogen

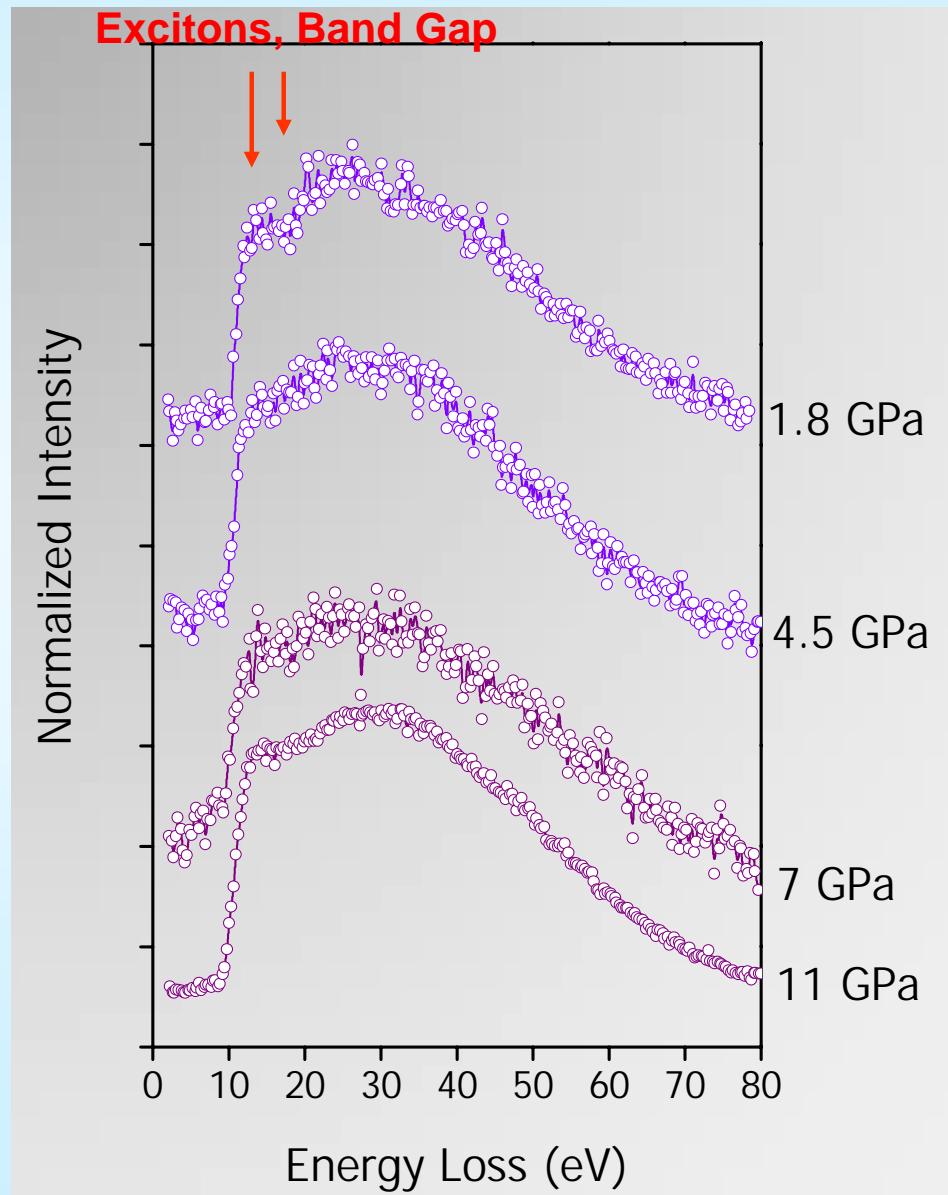
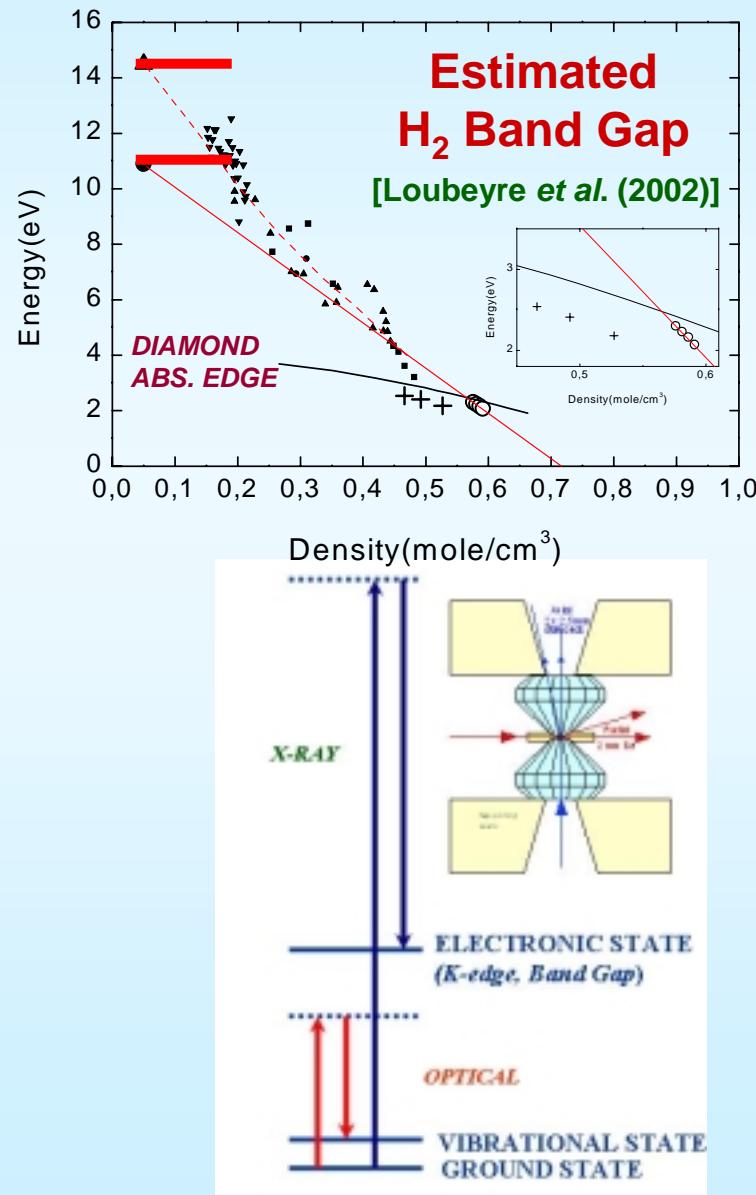


[Goncharov et al.,
Phase Transitions
(2007)]

- High pressure structures?
- Band gap and electronic properties?
- Liquid superconducting/superfluid ground state?

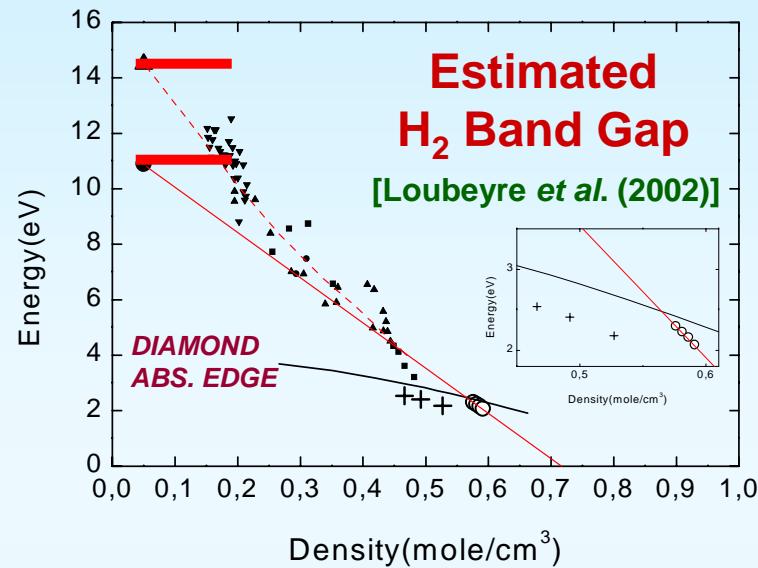


Direct measurements of the hydrogen band gap

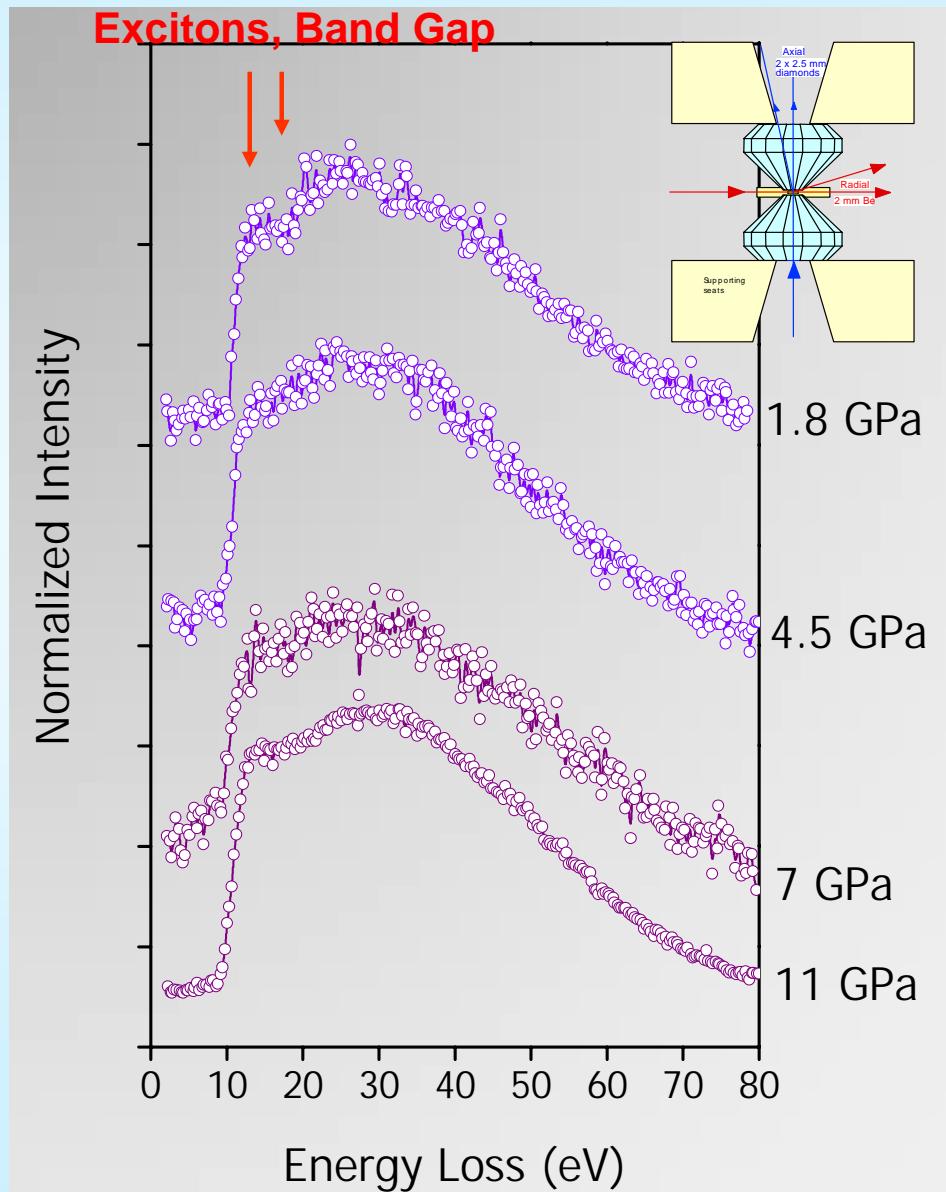




Direct measurements of the hydrogen band gap



- Extend to higher pressures
- Submicron beams/higher brightness





Predicted metallic superfluid

PRL 95, 105301 (2005)

PHYSICAL REVIEW LETTERS

week ending
2 SEPTEMBER 2005

Observability of a Projected New State of Matter: A Metallic Superfluid

E. Babaev

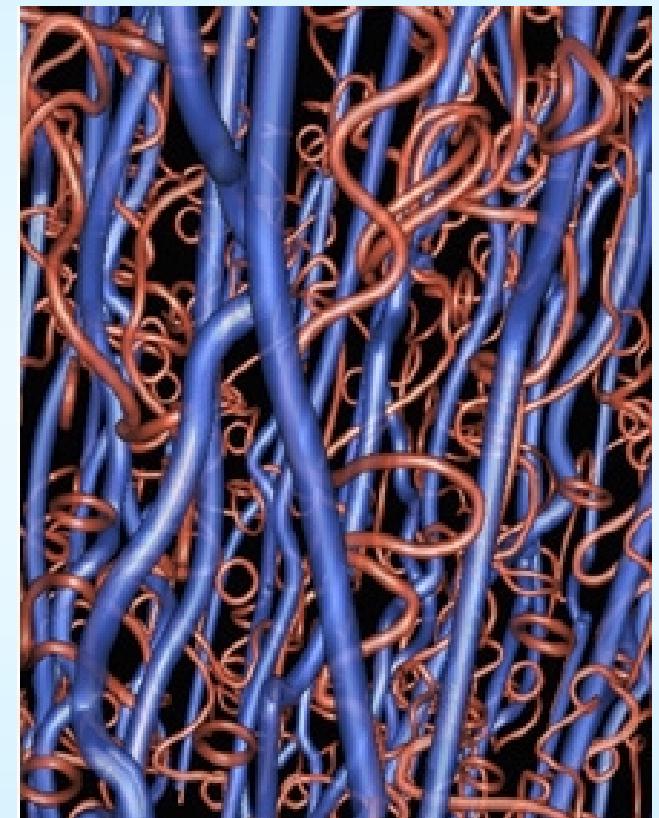
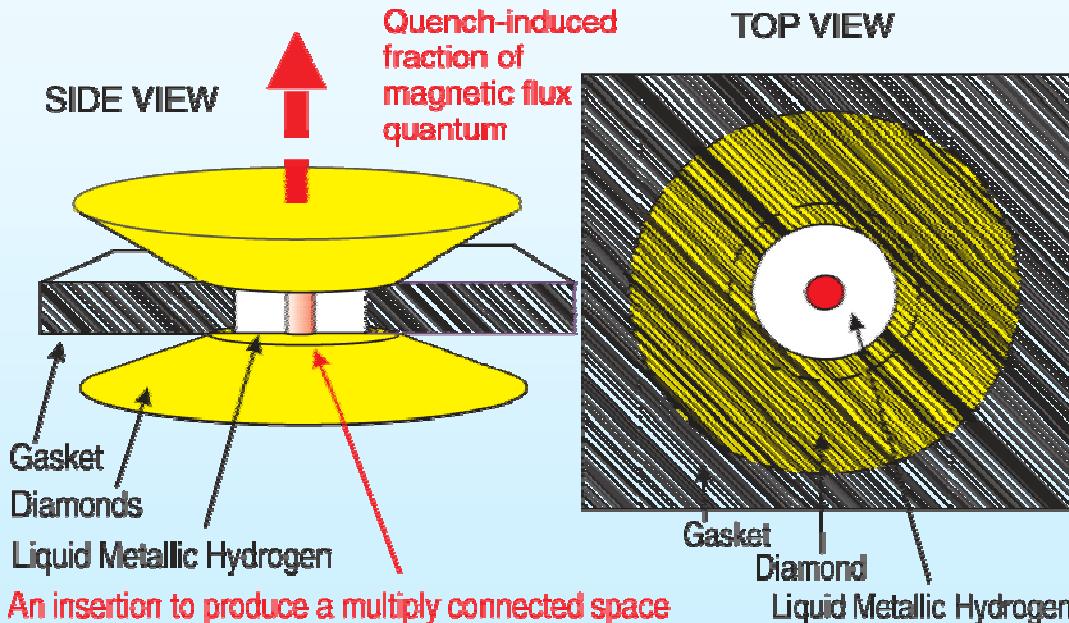
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA
 Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

A. Sudbø

Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA
 (Received 13 June 2005; published 1 September 2005)



- Can we create and image these structures?
- Combined P-T-H?

Hydrogen-rich systems under pressure: novel metals and superconductors?

1. HYDROGEN

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VOLUME 92, NUMBER 18

PHYSICAL REVIEW LETTERS

week ending
7 MAY 2004

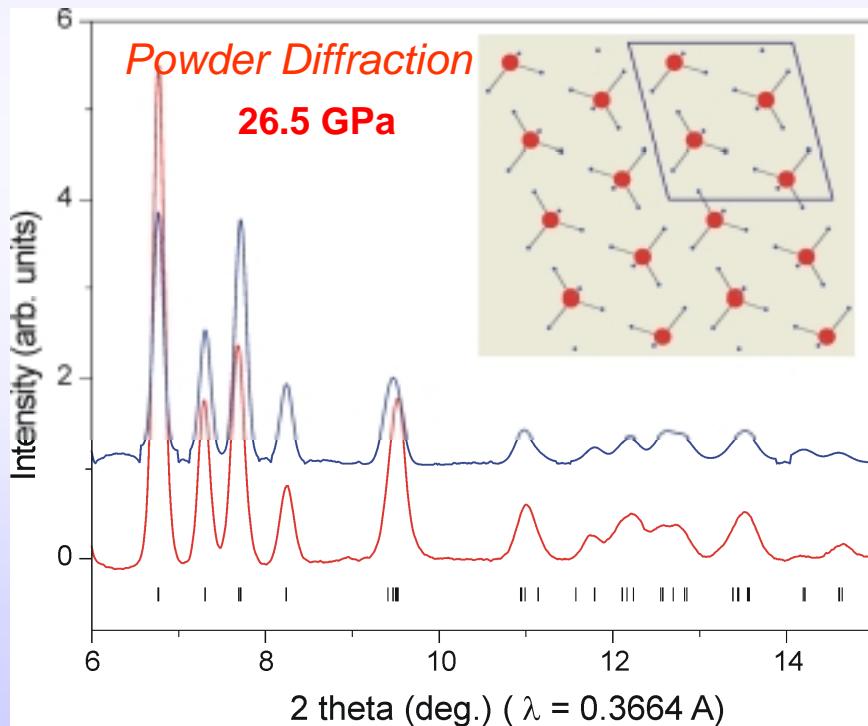
Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

N.W. Ashcroft

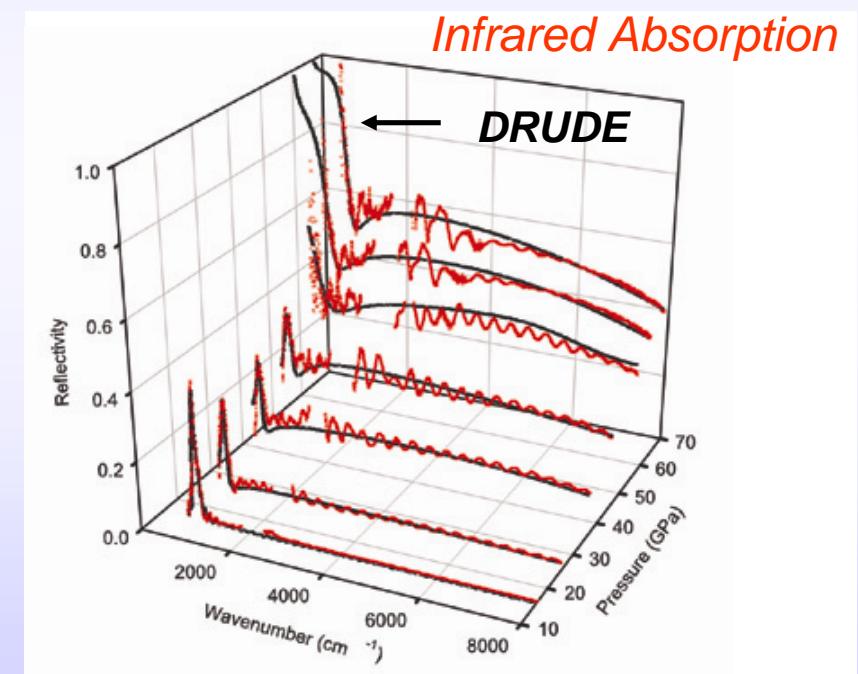
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA

Donostia International Physics Center, San Sebastian, Spain

(Received 29 December 2003; published 6 May 2004)



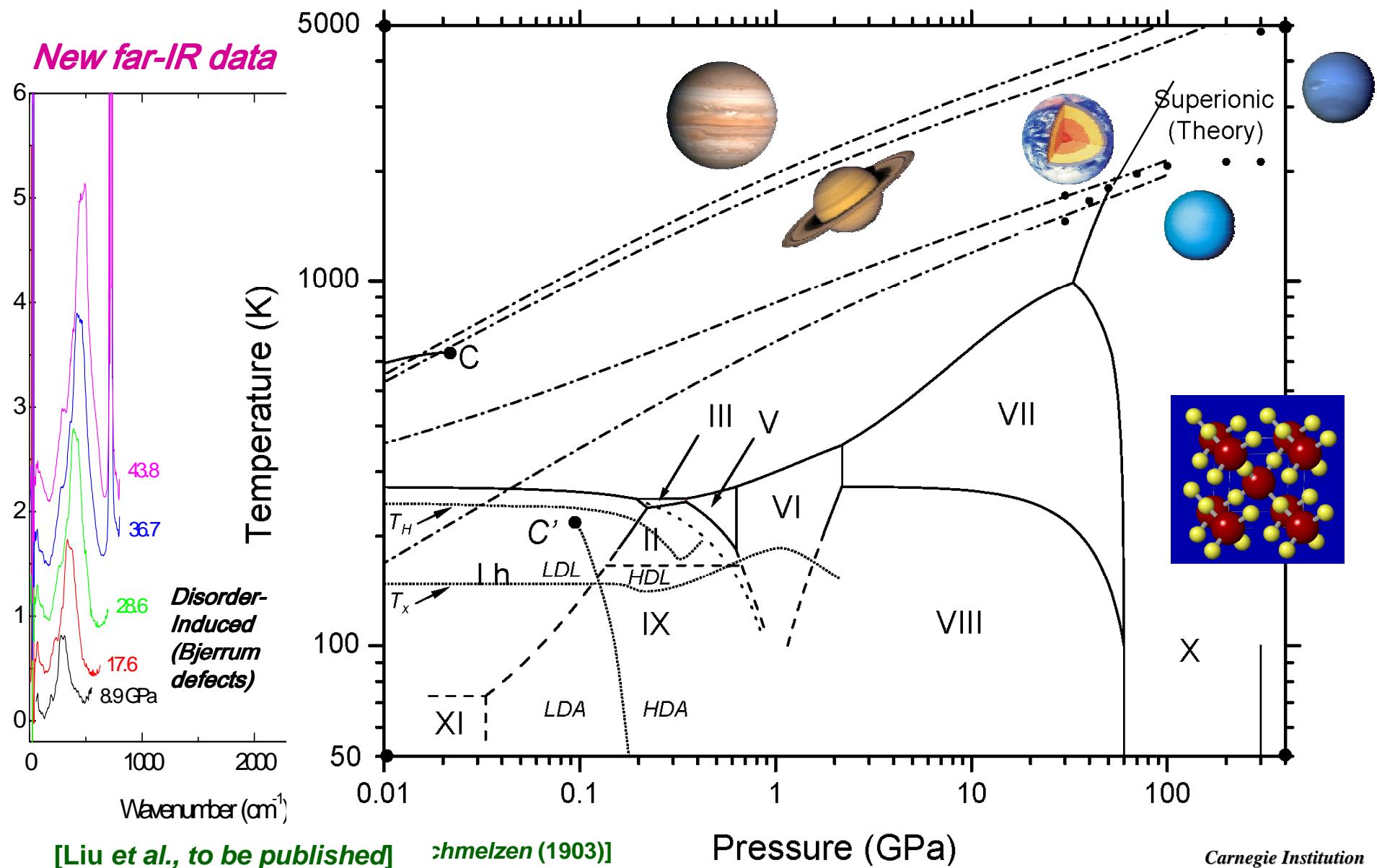
- SnBr_4 -type ($P2_1/c$)
- Stable to >60 GPa



- Insulator-metal transitions at 60 GPa
- Poor metal: possible high T_c

1. HYDROGEN

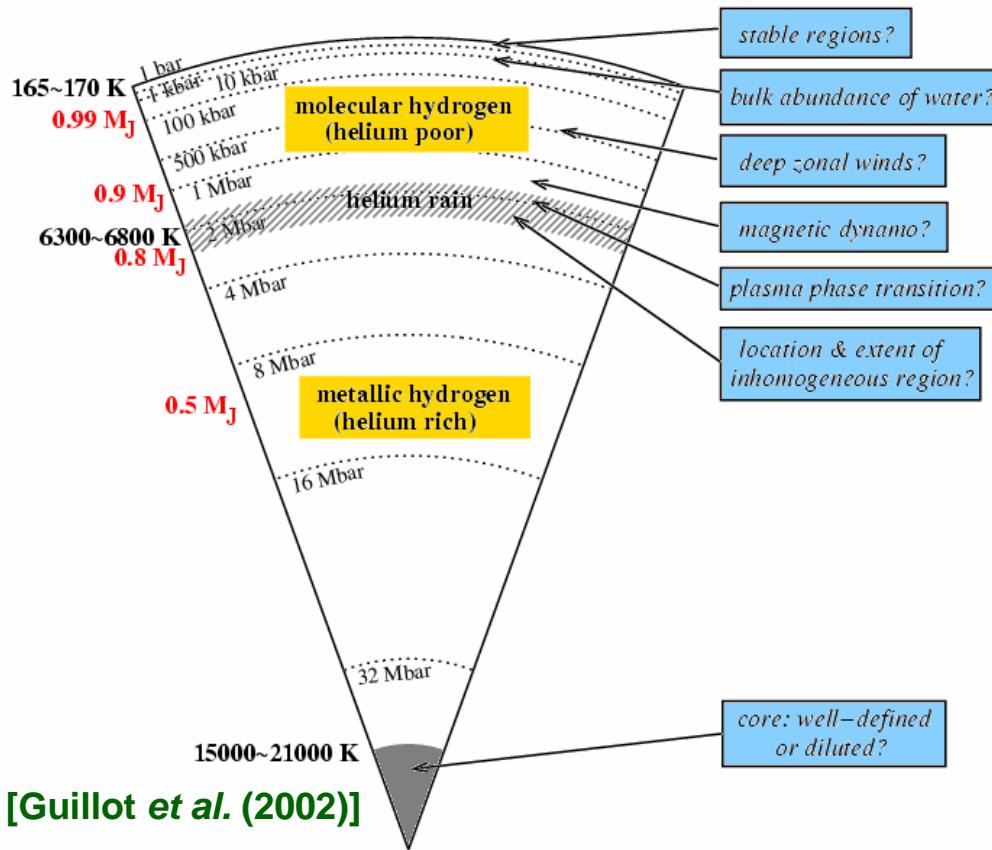
The behavior of water continues to present new questions



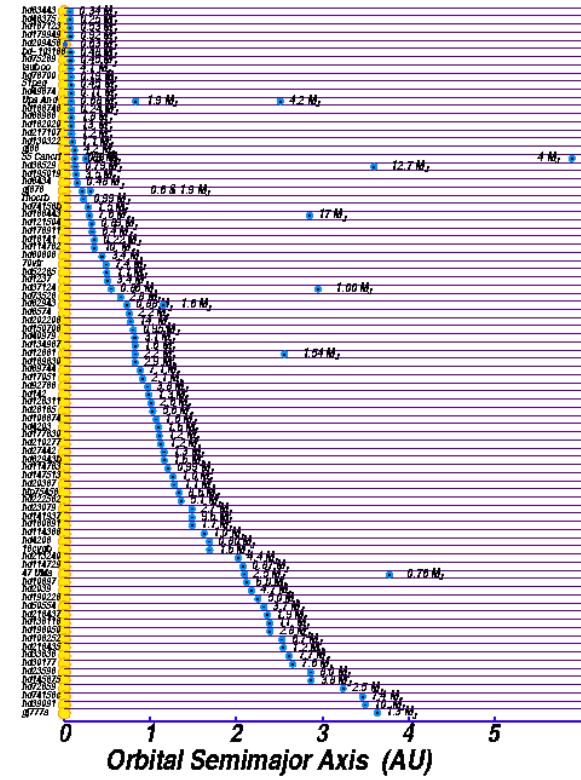
Understanding the high-pressure physics of hydrogen systems is essential for planetary science



Jovian Planet Interiors



Extrasolar Planets



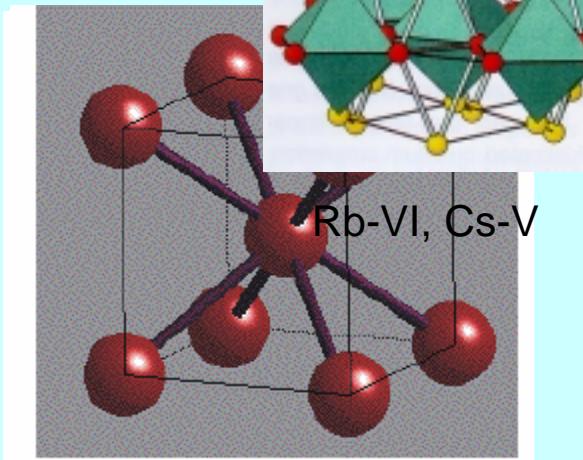
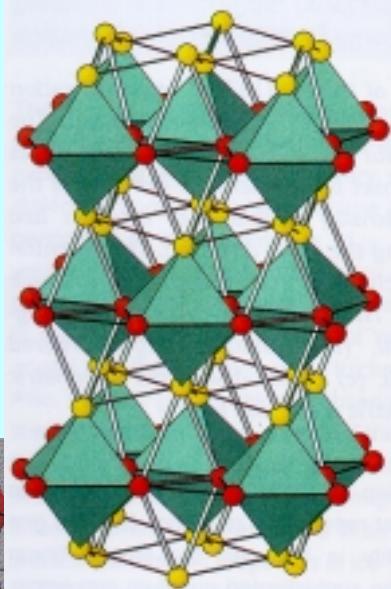
- Outer planet interior structures?
- Presence of a Jovian cores?
- Giant planet formation?
- Nature of exoplanets (e.g., super Earths)?

- Need Higher P and T
- New diagnostics
- Time-dependent probes

Pressure induced complexity in alkali metals

2. NOVEL METALS

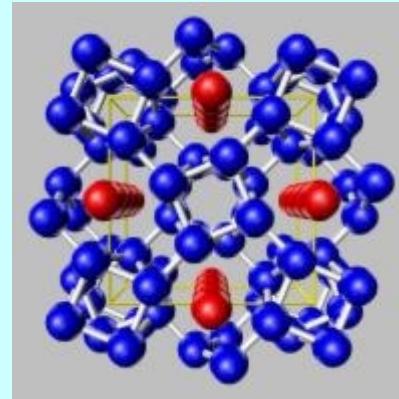
Li
Na
K
Rb
Cs



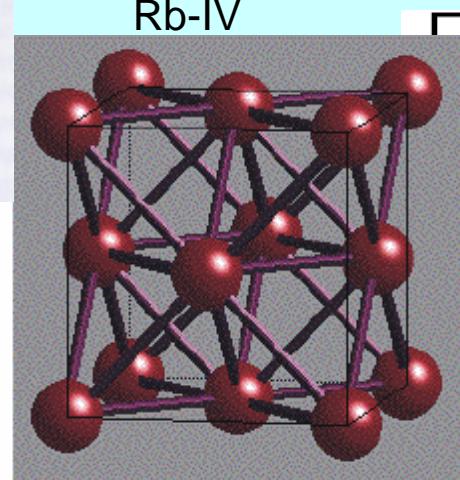
BCC Body-Centred Cubic

Ambient pressure

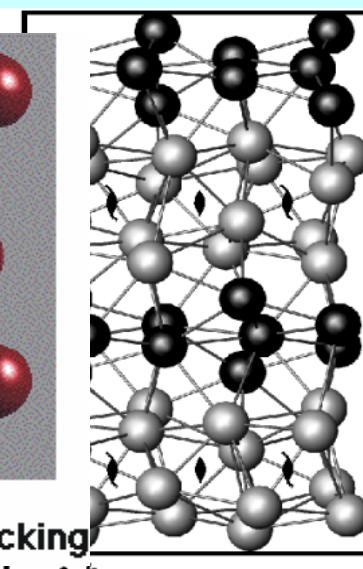
[McMahon & Nelmes (2006); Degtyareva *et al.*, to be published]



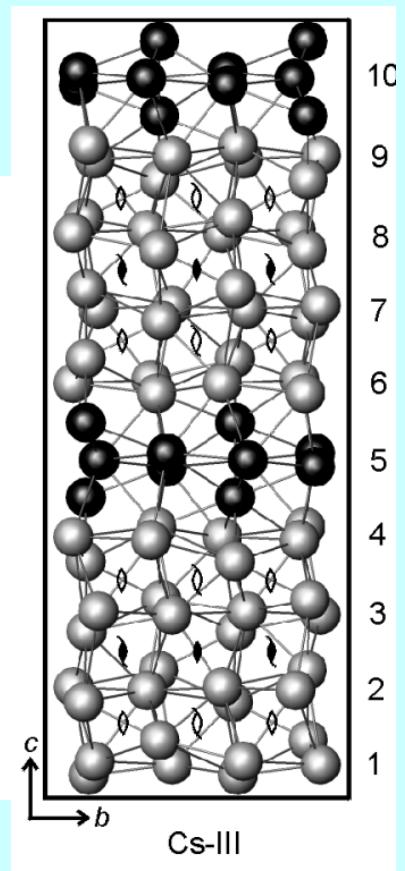
High Pressure



CCP Cubic Close-Packing

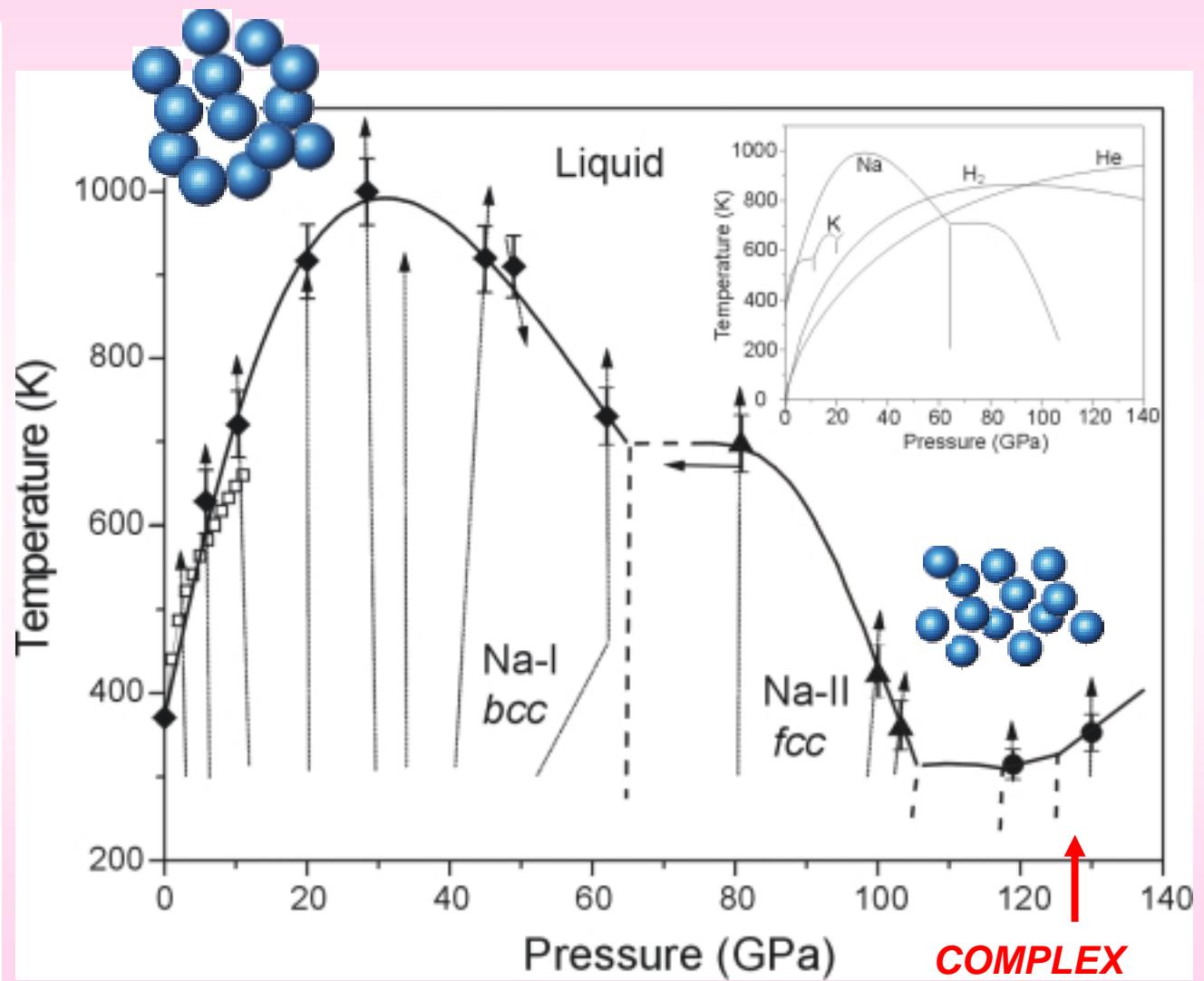
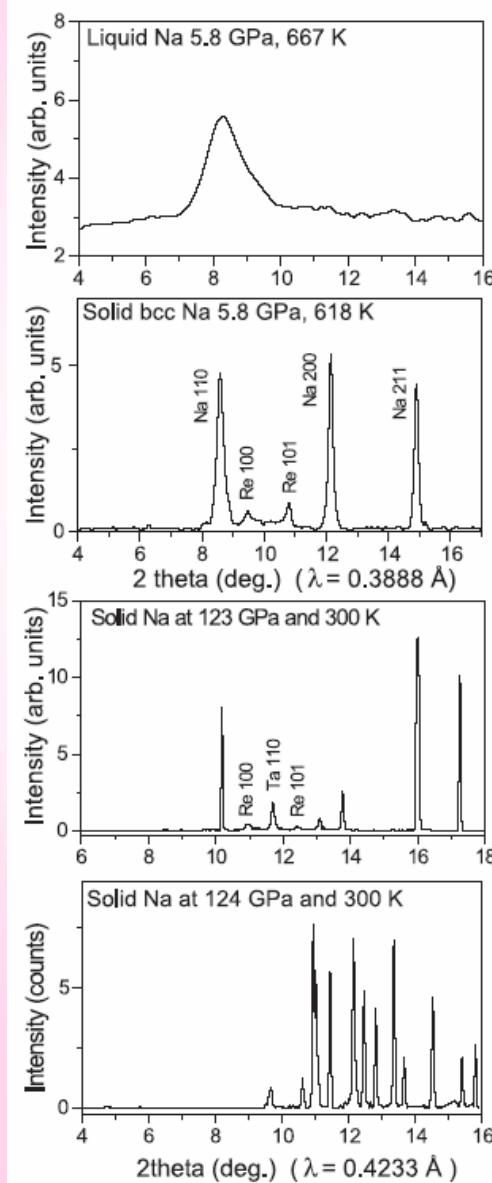


Rb-III



Cs-III

Sodium has a remarkable phase diagram



[Gregoryanz et al. Phys. Rev. Lett., 94, 185502 (2005)
also, Hanfland et al., to be published]

**COMPLEX
STRUCTURES
8 new phases!**

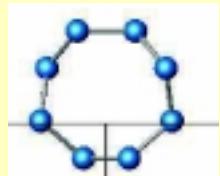
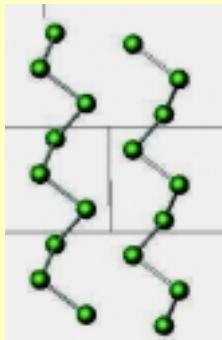
Structures and superconductivity in Group VI elements under pressure

2. NOVEL METALS

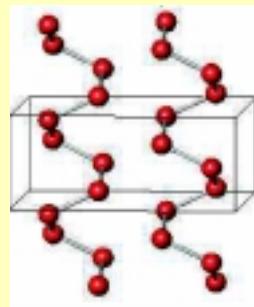
CDAC 

SULFUR

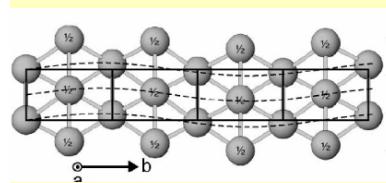
7 GPa



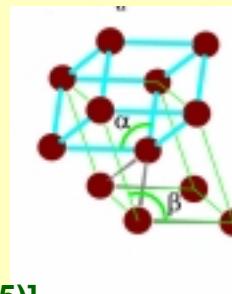
15 GPa



90 GPa



160 GPa



T_c (K)

18

16

14

12

10

8

6

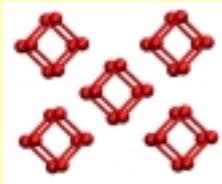
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2

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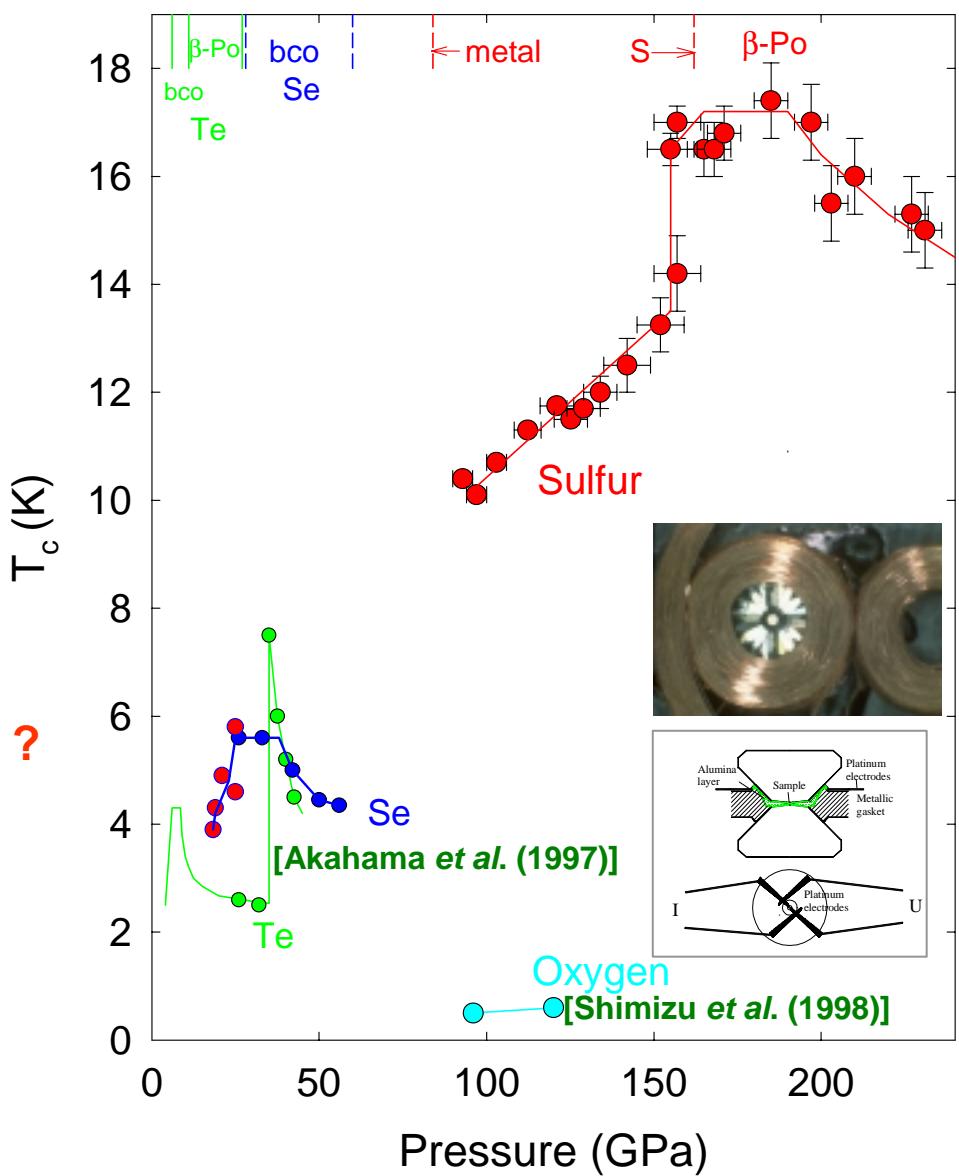
[Degtyareva et al., *Nature Mat.*, (2005)]

OXYGEN



?

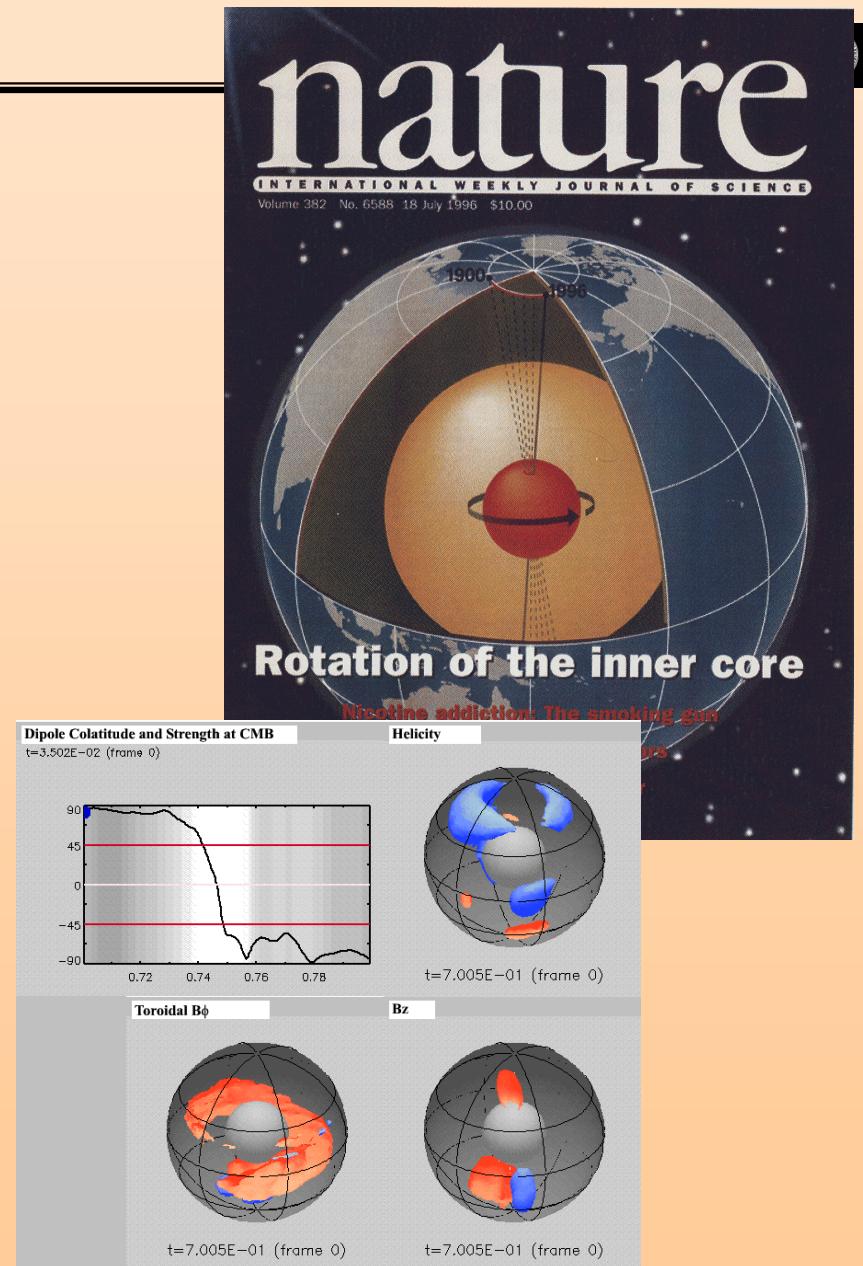
[Lundsgaarde et al., *Nature* (2006)]



New findings and phenomena in iron under pressure

2. NOVEL METALS

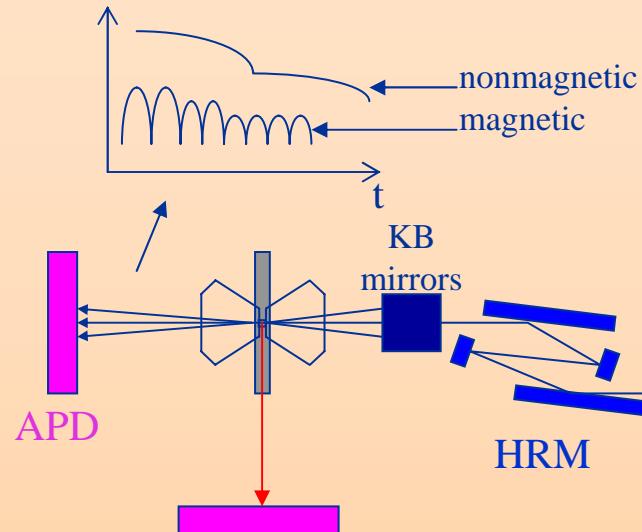
- High *P-T* polymorphism
[Boehler (2000); Dubrovinsky *et al.* (2001);
Ma *et al.* (2004); Price *et al.* (2005)]
- Elasticity/plasticity/strength
[Singh *et al.* (1998); Merkel *et al.* (2004);
Woortman *et al.* (1998); Mao *et al.* (1998)]
- Structure of liquid
[Sanloup *et al.* (2000); Shen *et al.* (2004)]
- Magnetic properties
(superconductivity; ferromagnetism)
[Shimizu *et al.* (2001); Steinle-Neumann *et al.*
(2002); Mazin and Singh (2002)]
- Pressure-induced reactions
FeH, Fe(Xe), Fe(K)
(Mg,Fe)O, (Mg,Fe)SiO₃
[Badding *et al.* (1991); Caldwell *et al.* (1997);
Lee *et al.* (2003), Mao *et al.* (2004),
Dubrovinsky *et al.* (2001)]



High P - T spectroscopies of Fe: Nuclear Resonance inelastic x-ray scattering

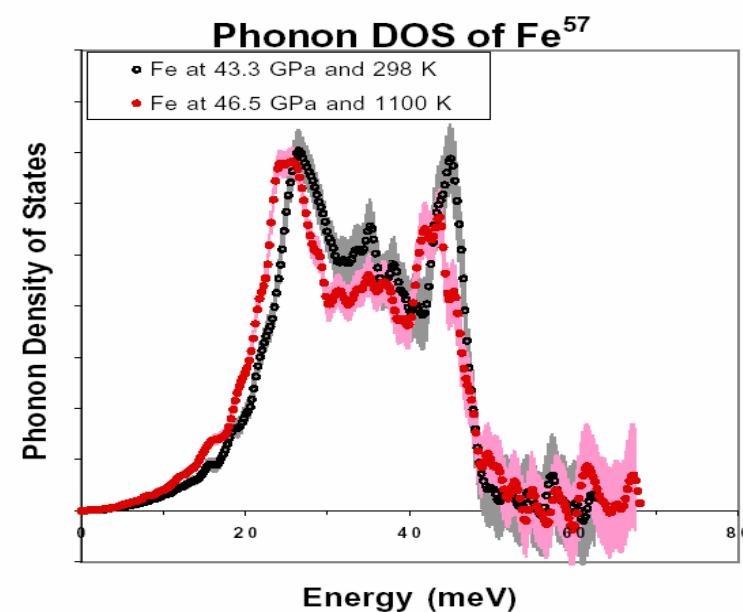
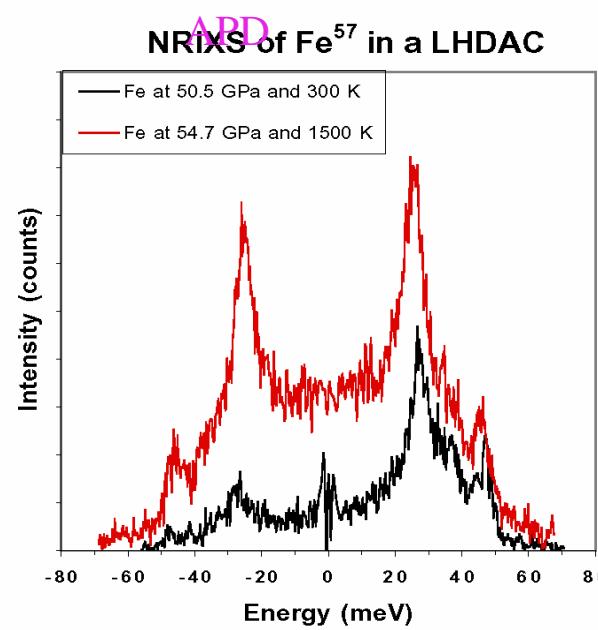
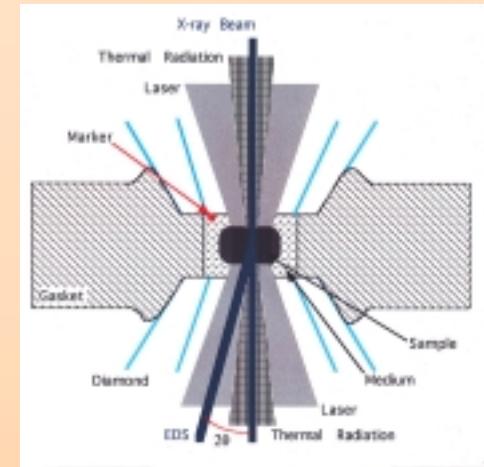
2. NOVEL METALS

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[Lin et al., Geophys. Res. Lett. (2004); Science (2005)]

- Calibration of Temperature



$$\frac{K_S}{\rho} = V_P^2 - \frac{4}{3} V_S^2$$

$$\frac{G}{\rho} = V_S^2$$

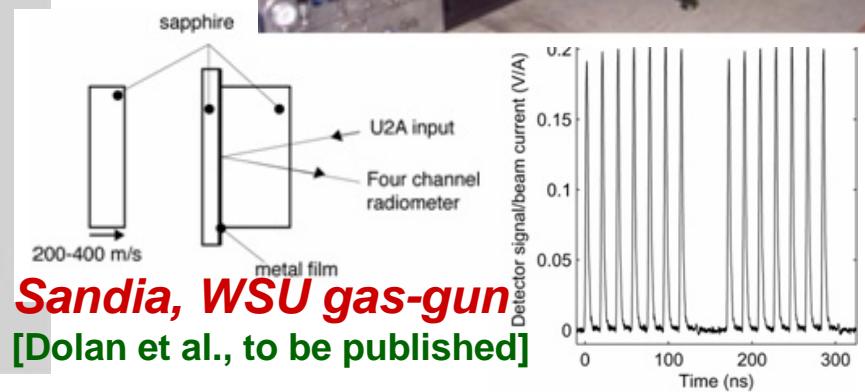
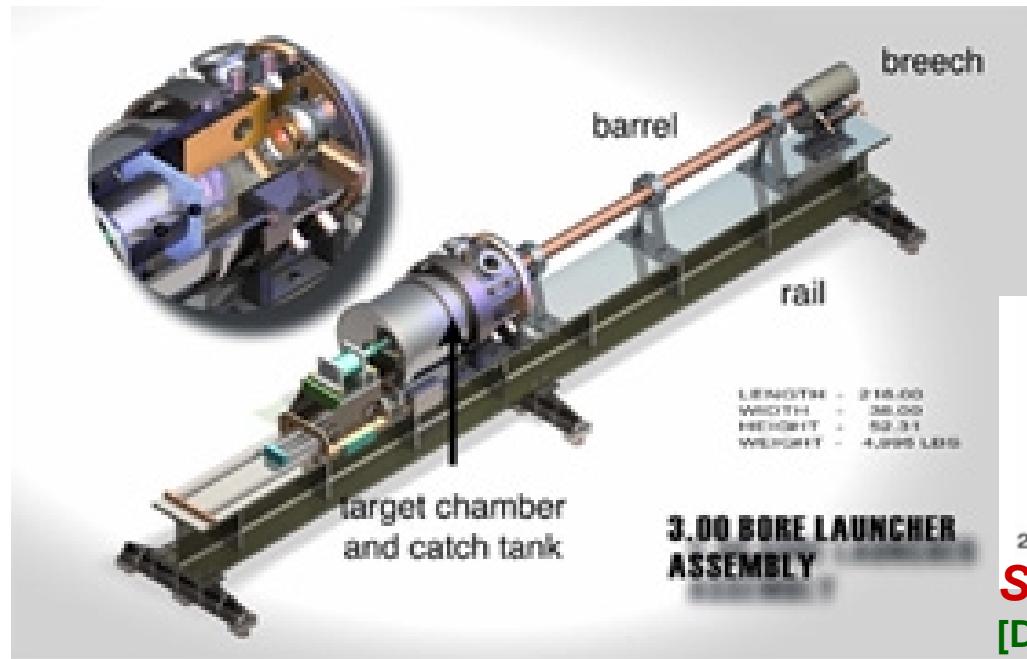
$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3}$$

- High P - T sound velocities

Dynamic compression studies of metals: first synchrotron measurements

CDAC 

- Time resolved IR reflectivity at U2A (NSLS) for temperature calibration (to 8 GPa)



- X-ray diffraction of shock compressed simple metals to 20 GPa at Sector 16 (APS)

WSU powder gun
[Gupta et al., to be published]

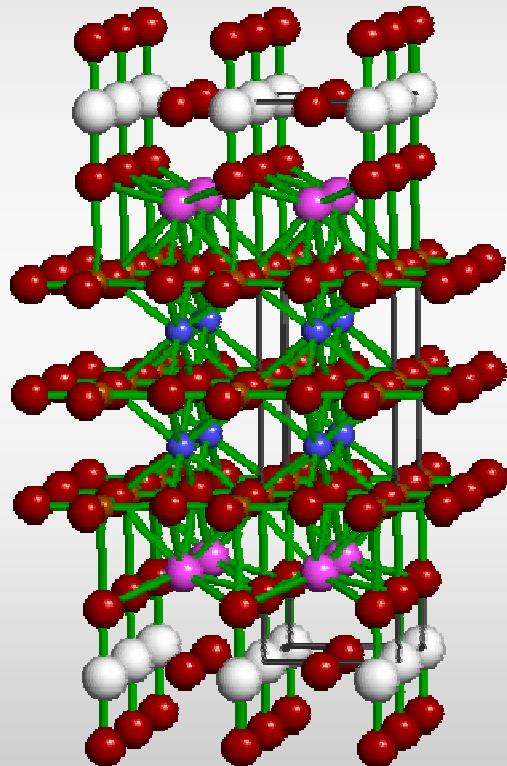
- Polycrystals/fluids?
- Higher P-T conditions?
- Prospects for NSLS II?

Novel behavior in oxides under pressure

3. OXIDES

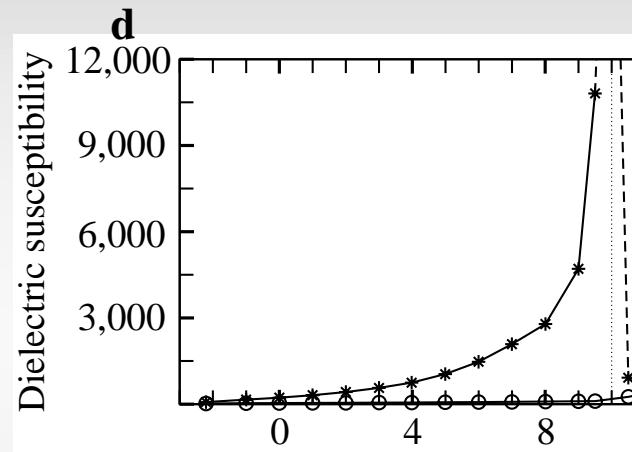


Highest Temperature Superconductivity
 $T_c = 164\text{ K}$ at 30 GPa

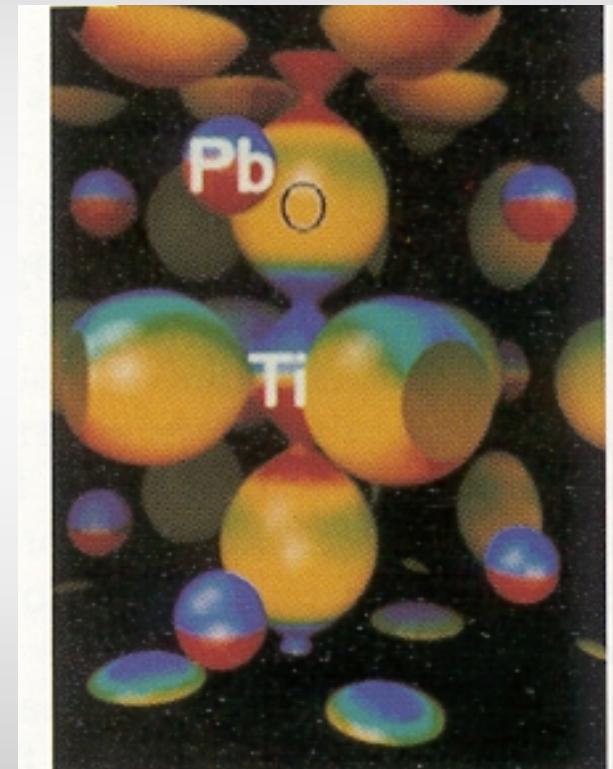


[Gao et al. *Phys. Rev. B* (1994);
Lokshin et al. *Physica* (2002)]

Colossal Enhancements of Piezoelectricity Predicted



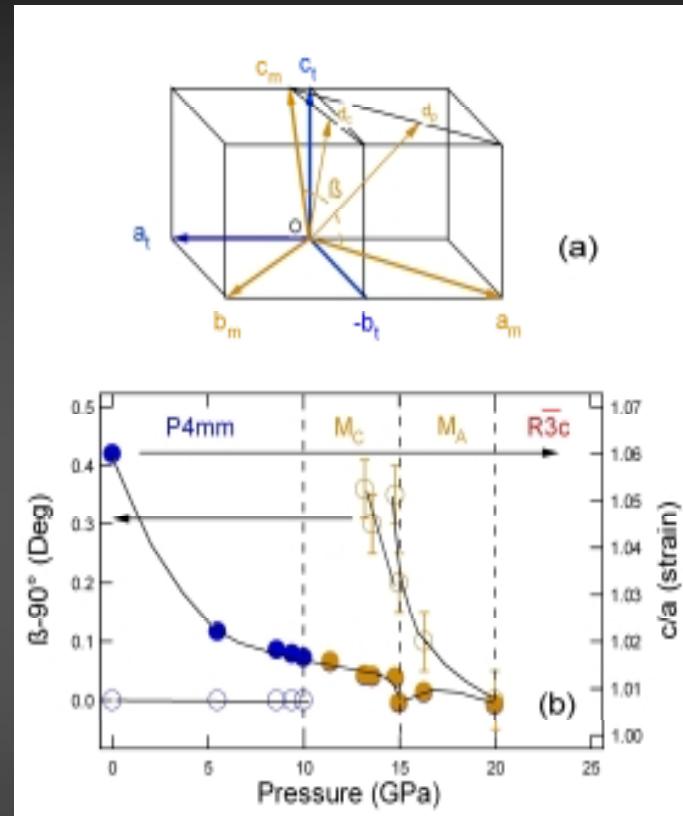
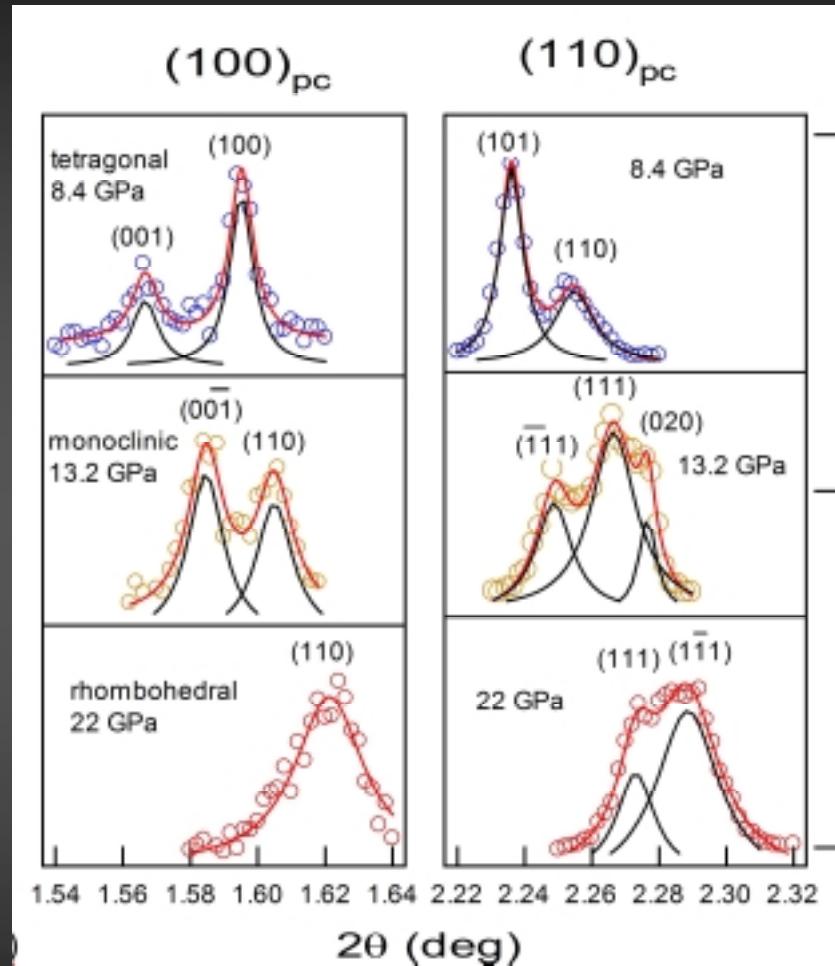
Predicted in ‘simple’ materials: PbTiO_3



[Wu and Cohen, *Phys. Rev. Lett.* (2005)]

➤ *Test of high T_c mechanisms*

Predicted structural transitions PbTiO_3 were confirmed by high resolution x-ray diffraction



$\text{P}4\text{mm}$ (tetragonal) 0 – 10 GPa;
 Pm (monoclinic) 10 – 15 GPa;
 Cm (monoclinic) 15 – 20 GPa;
 $\text{R}-3\text{c}$ (rhombohedral) >20 GPa

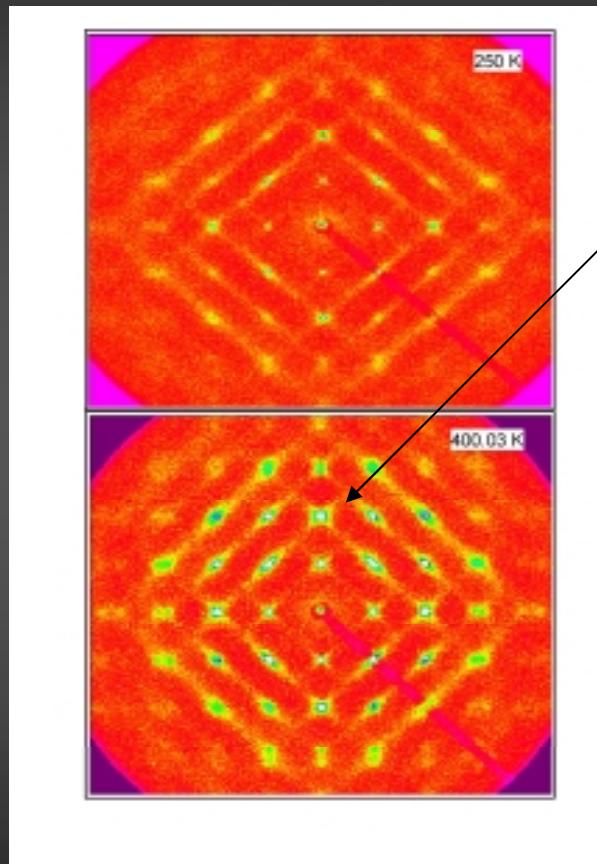
- cryogenic diffraction (10 K)
- powder sample in Ne medium
- Sectors 11 & 16 APS

➤ Complex solid solutions not needed for enhancements

Diffuse x-ray scattering is an additional indication of large dielectric response: PSN

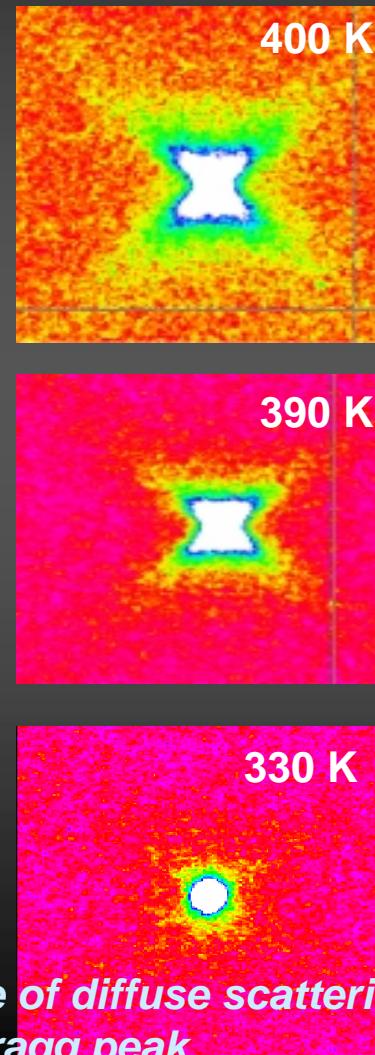
3. OXIDES

PSN 001 cut

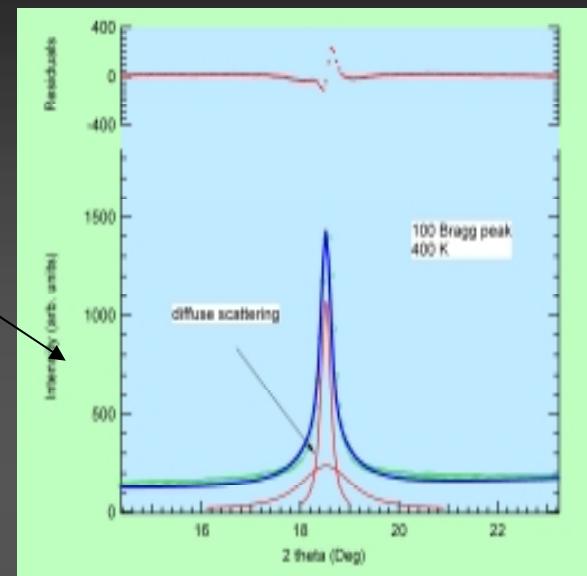


Carnegie Institution

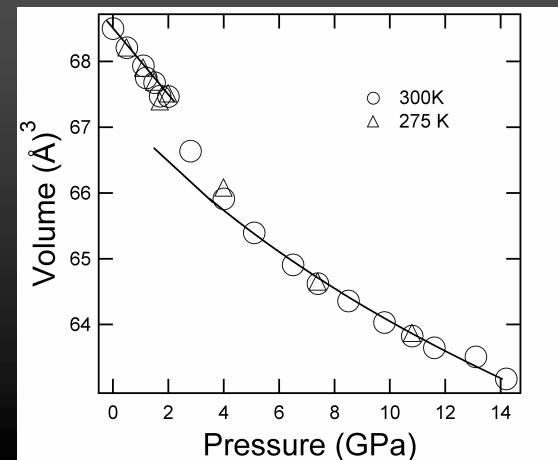
(100) Bragg peak



T-dependence of diffuse scattering around 100 Bragg peak

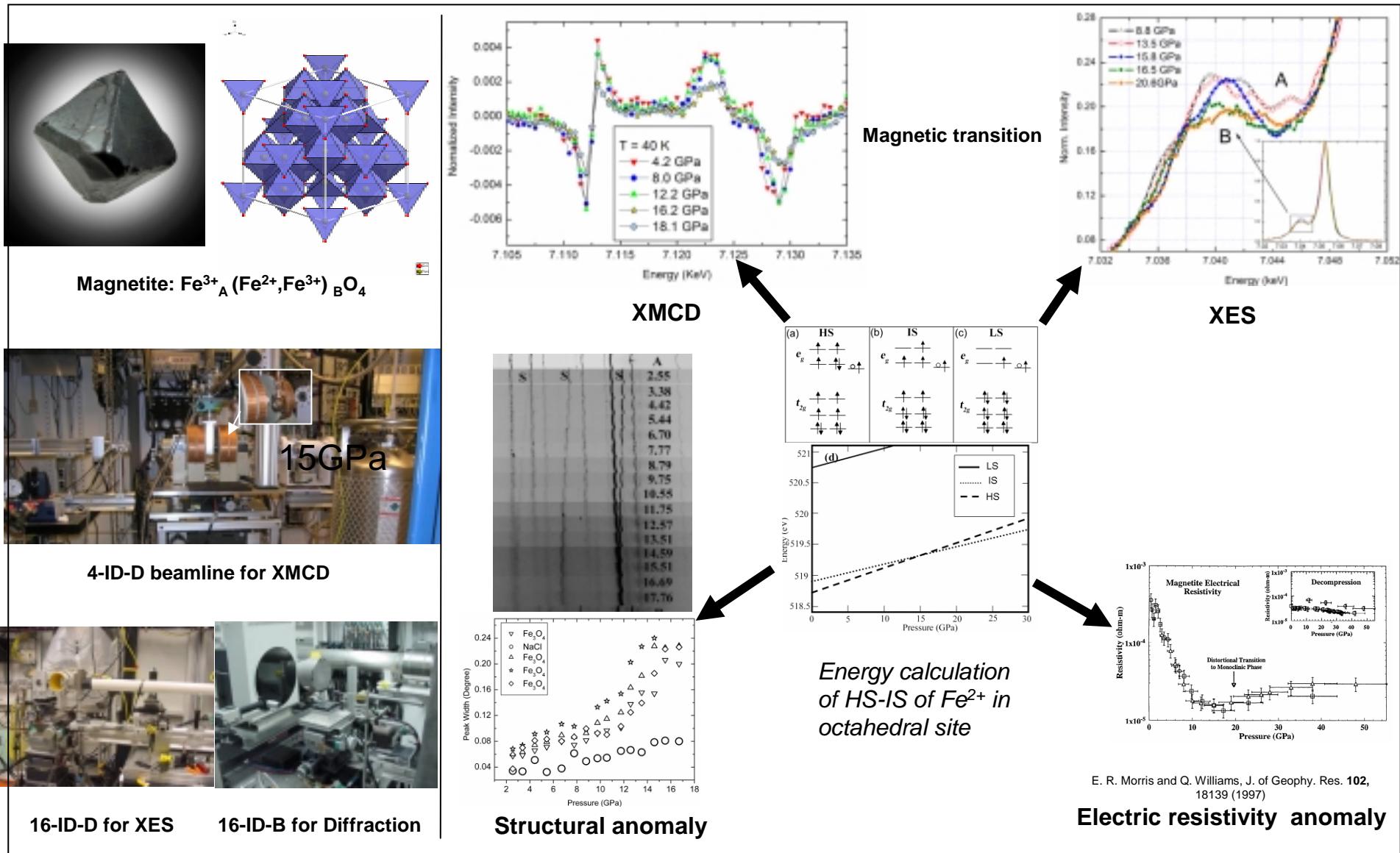


Lorentzian and Gaussian fit to the diffuse scattering



Novel pressure-induced magnetic transition in magnetite: use of complementary techniques

3. OXIDES



[Ding *et al.*, Phys. Rev. Lett. (2008)]

Complex materials at the nanoscale: Shock processing, nanomineralogy, textured materials

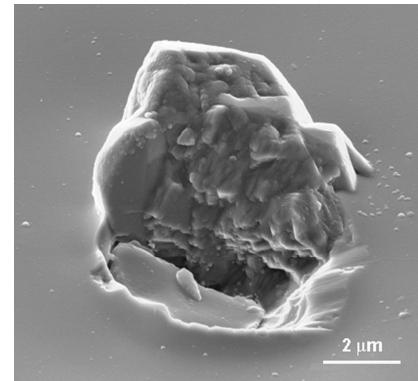
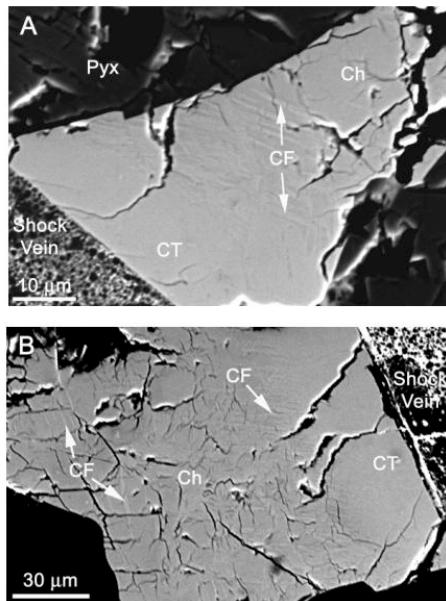
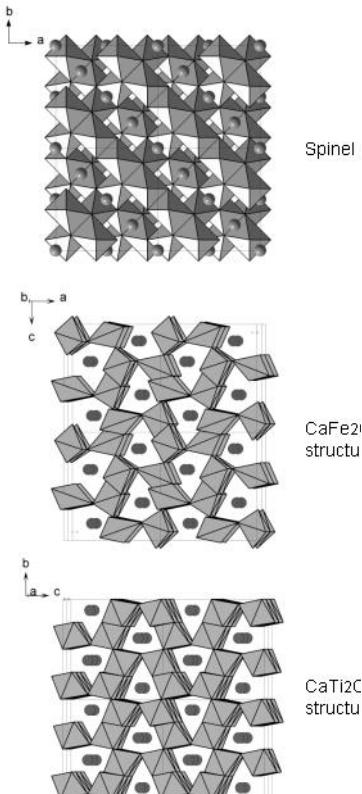
3. OXIDES

CDAC

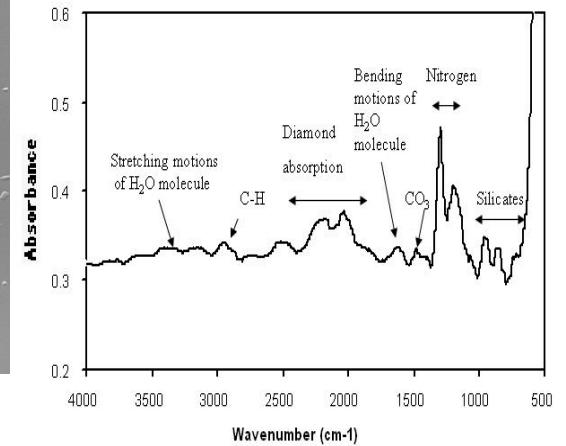


Two new minerals, high-pressure forms of chromite, discovered in shocked meteorite & synthesized in DAC

[Chen et al., PNAS (2003)]

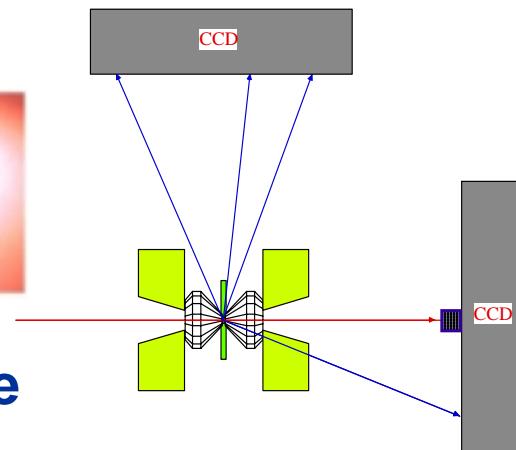


Infrared spectroscopy of microdiamonds in zircon



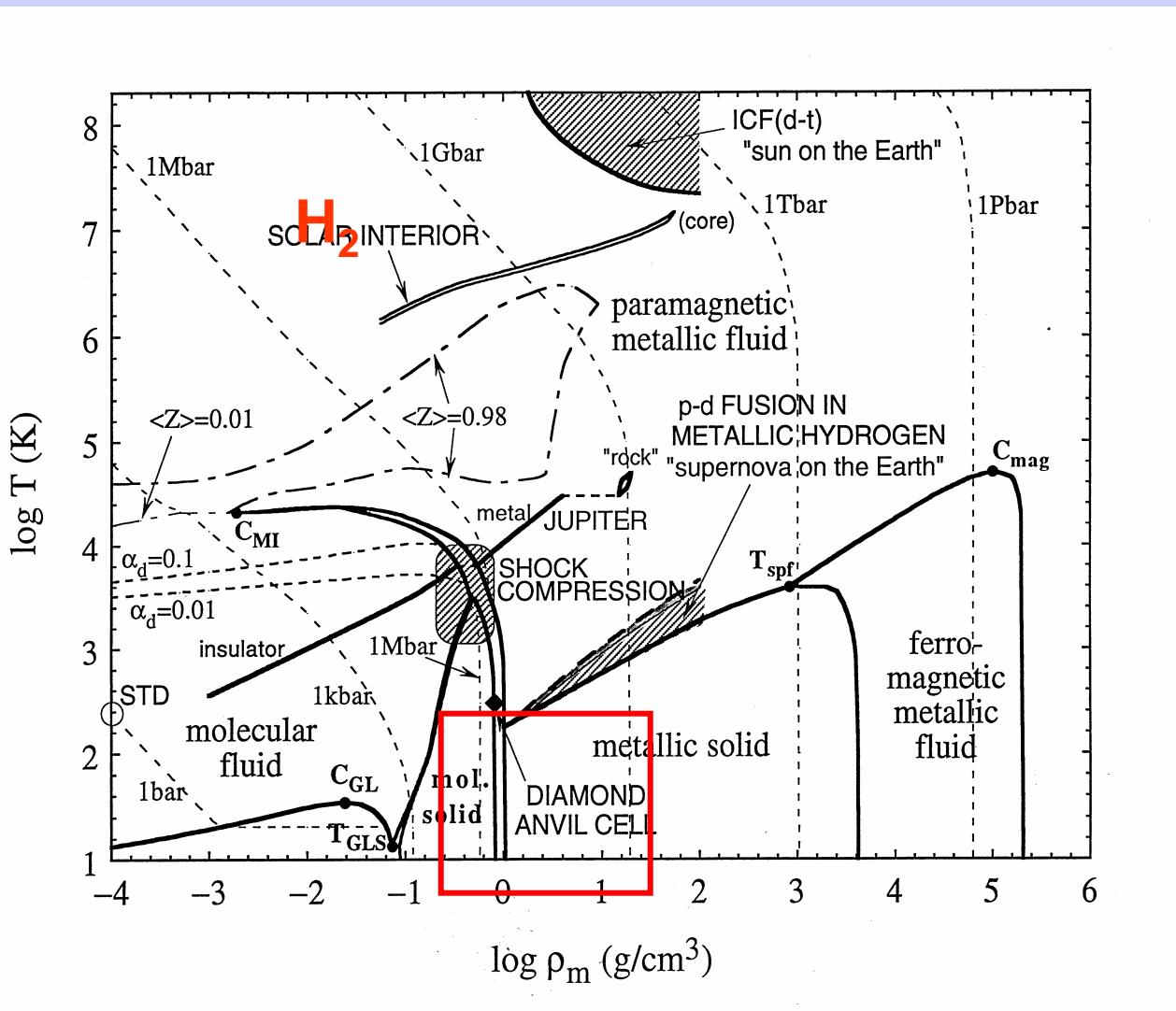
[Dobrzhinetskaya et al., EPSL (2007)]

Panoramic cells for submicron Laue diffraction and spectroscopy



We are exploring only a limited domain of P - T space

CDAC 



[Ichimura, *Phys. Reports* (1995)]

Theoretical Predictions
UNCHARTED TERRORY

- Higher pressures (1 TPa or 10 Mbar) and temperatures (>1 eV)

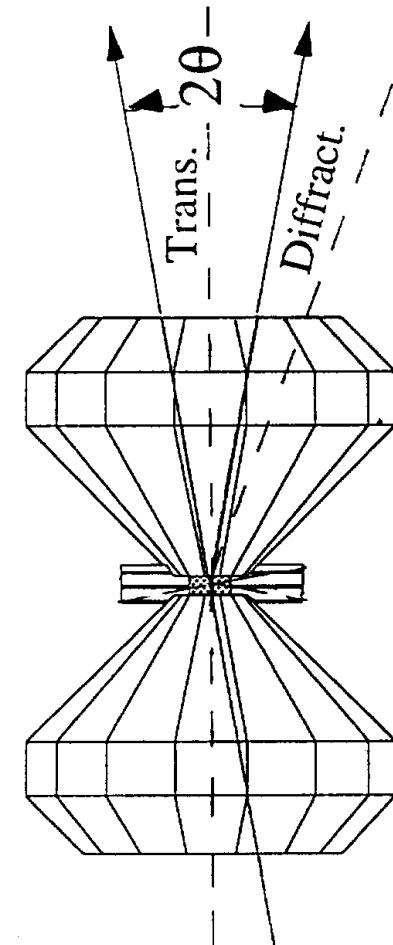
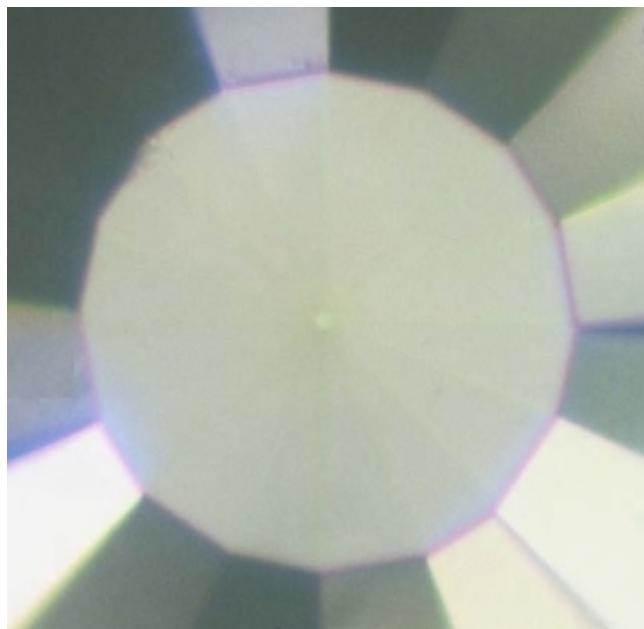
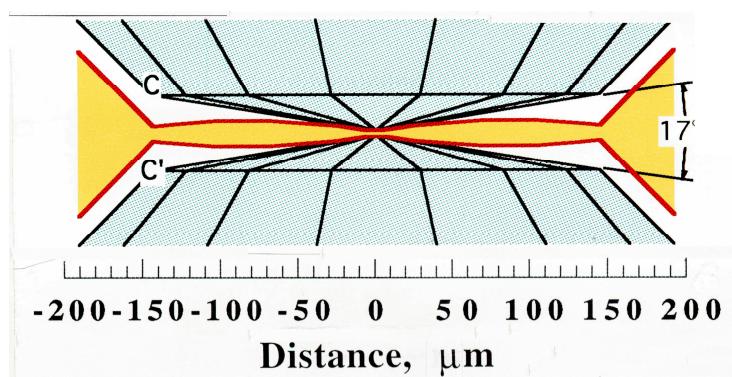
- Larger sample volumes needed (x-ray inelastic scattering, imaging THz spectra >100 GPa)

- Further improve accuracy/precision and applications of multiple simultaneous

- Combined static/dynamic compression (100 TPa; and >100 eV)

Toward higher pressures: x-ray radiography of the diamond deformation above 300 GPa

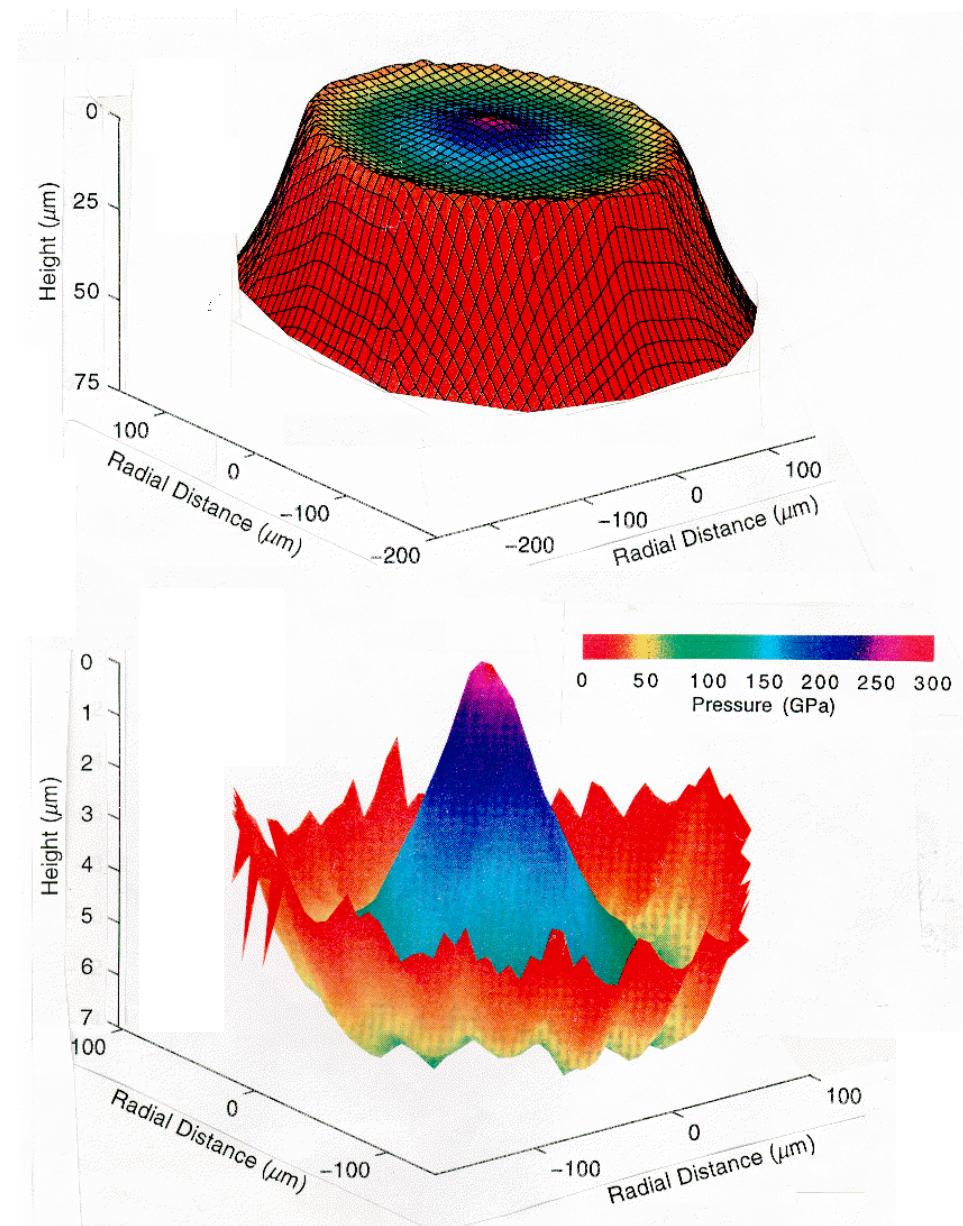
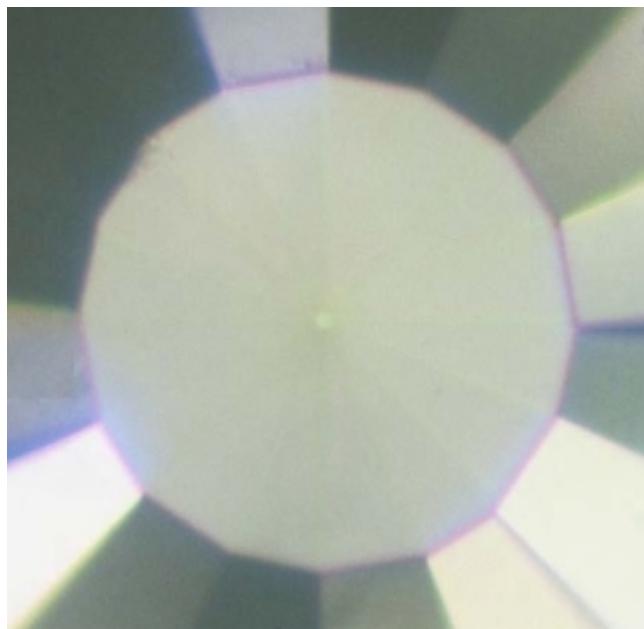
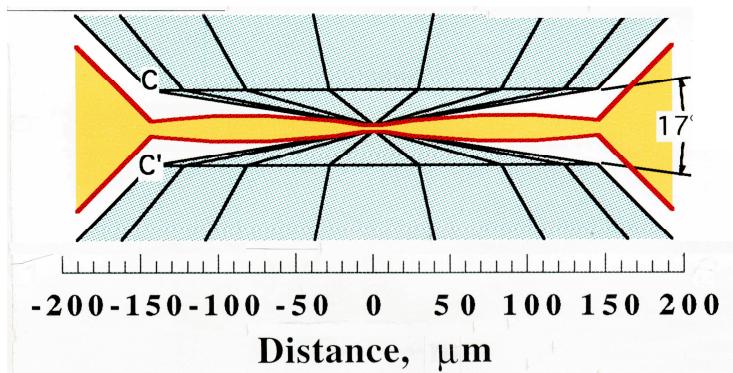
[Hemley, *Science*, 276, 1242 (1997)]



- White Beam ESRF (ID9)
- Simultaneous x-ray Diffraction (for pressure)

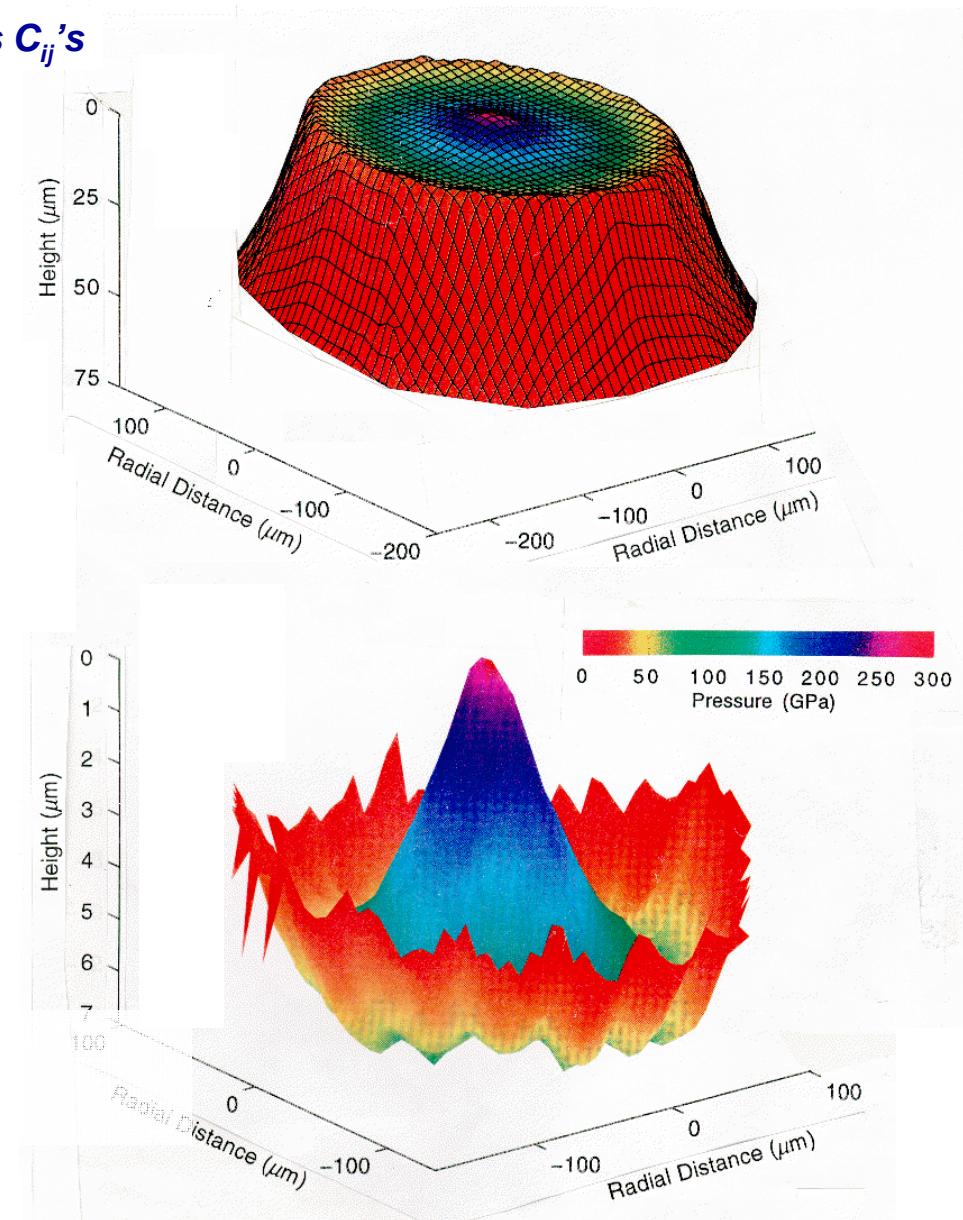
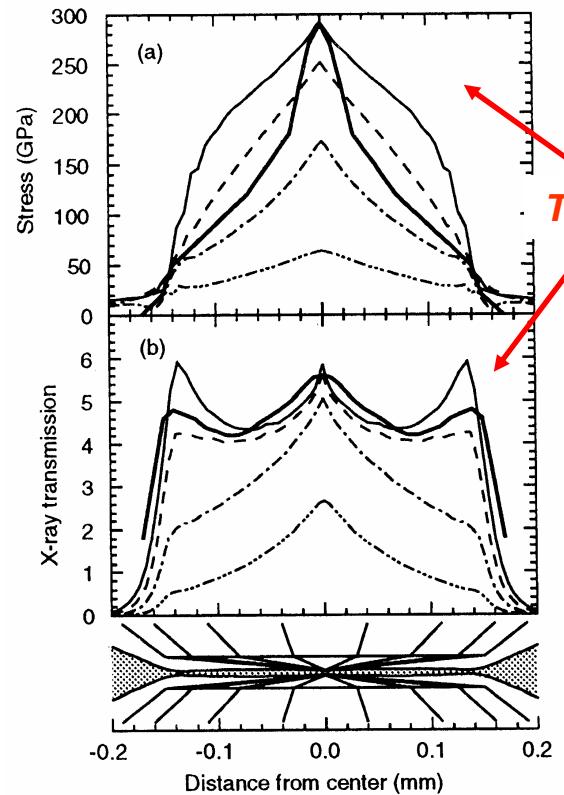
Toward higher pressures: x-ray radiography of the diamond deformation above 300 GPa

[Hemley et al., *Science* (1997)]



Toward higher pressures: x-ray radiography of the diamond deformation above 300 GPa

Finite Element Calculations: *First Principles C_{ij}*'s

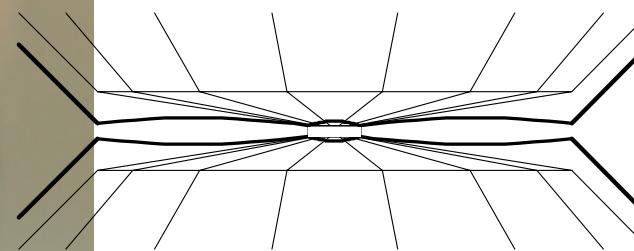
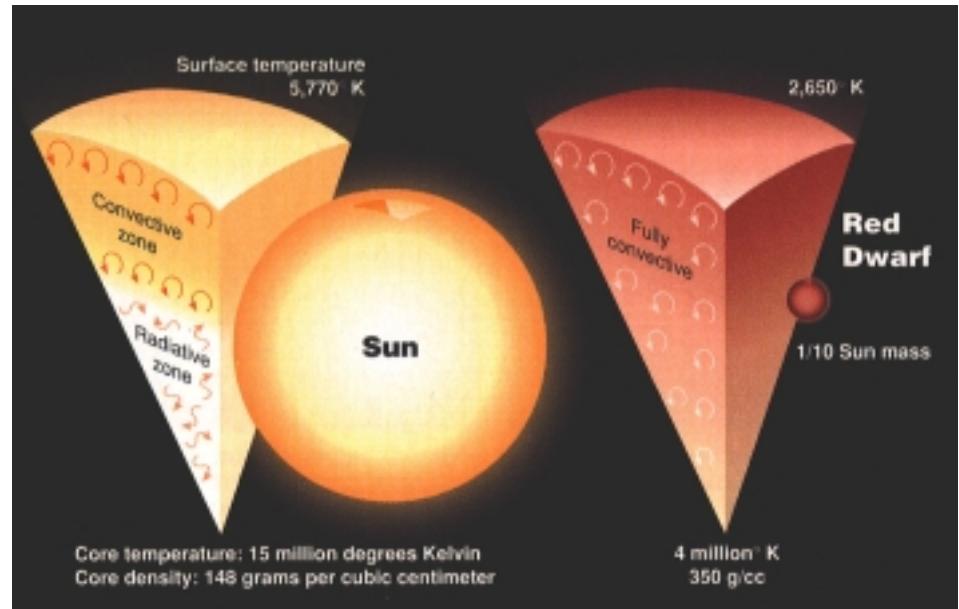
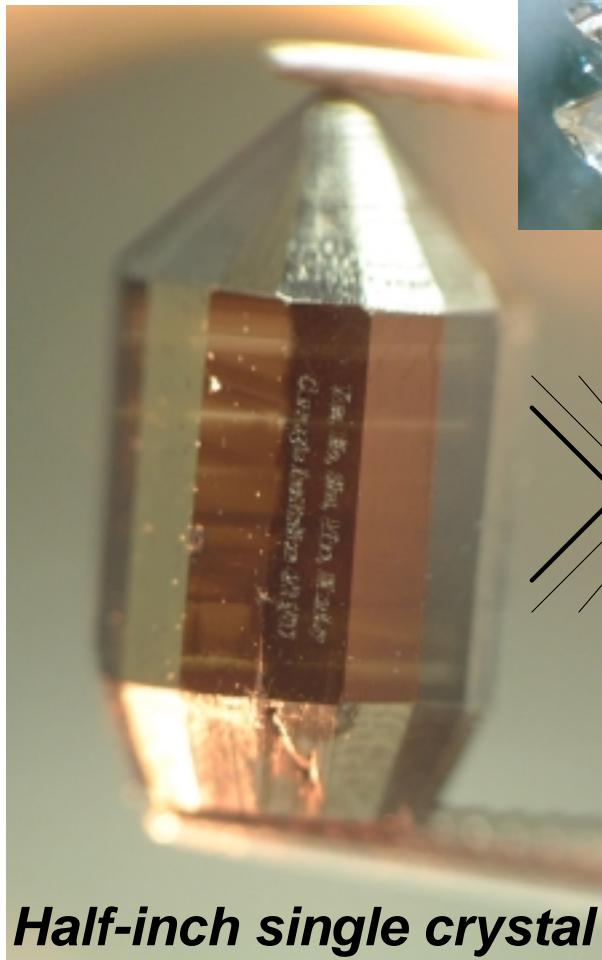


[Merkel et al. *Appl. Phys. Lett.* (1999)]

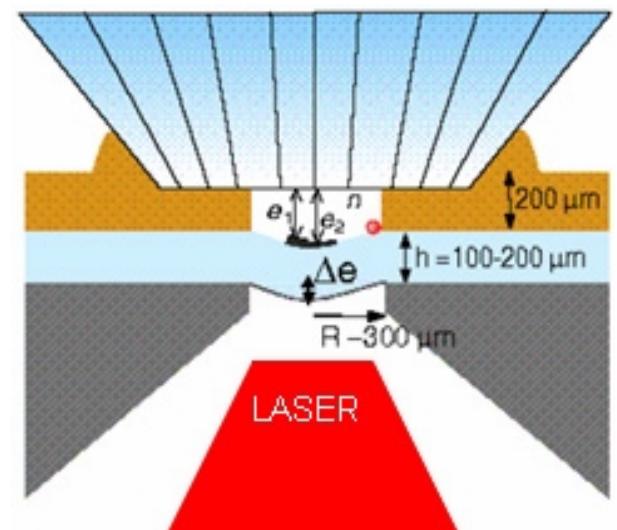
- **Nanoprobe diffraction**
- **3D imaging for higher pressures**

Extending the *P-T* range with static and dynamic compression

- Very large anvils
- Shaping diamond
- Embedded circuits



Combined
static/dynamic
compression
➤ *Gigabar*
pressures?



[Ho et al. *Indus. Diam. Rev.* (2006)]

Next generation high-pressure experiments at NSLS II



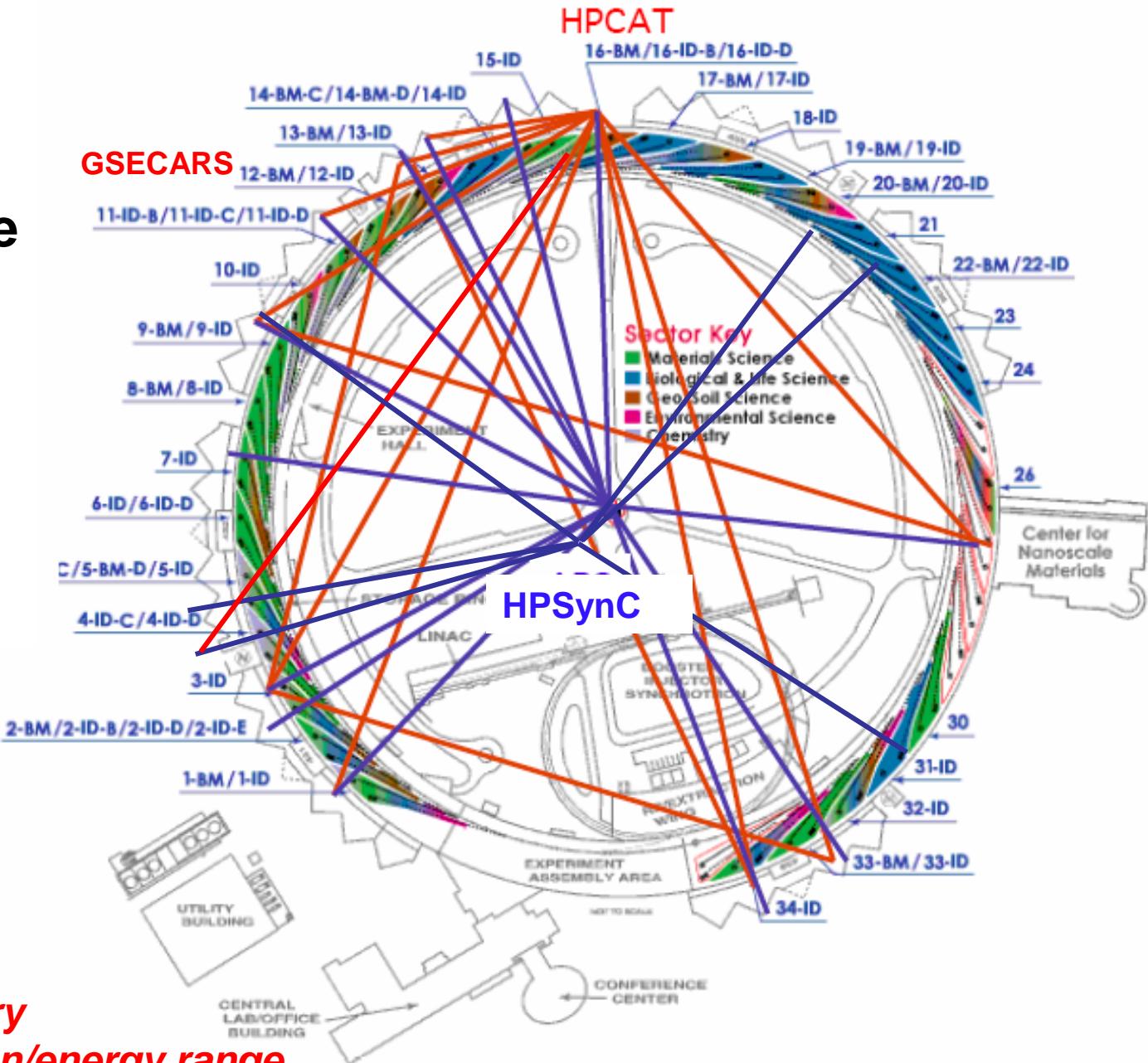
- ***Inelastic scattering in new P-T domains***
- ***Time dependent (<ps-scale) diffraction***
- ***Heterogeneous/complex assemblages: nm-diffraction***
- ***Interfaces/grain boundaries under pressure***
- ***Extending P-T-t***

Synergistic Approach to High-Pressure Synchrotron Research:

HPSynC APS

UTILIZE OPTIMIZED BEAMLINES

- *Energy resolution*
- *Energy range*
- *Detection geometry*
- *Analyzer resolution/energy range*
- *Collimation/focusing*



SCIENCE OUTLOOK

CDAC 

1. High pressure: a superb application of synchrotron x-ray and IR techniques, complementing other methods.
2. An essential tool for uncovering new physics and chemistry of materials under extreme conditions.
3. Numerous problems that span the sciences can now be addressed for the first time.
4. Particularly important are new far-IR developments, nanodiffraction, and inelastic scattering techniques.
5. Numerous new high-pressure technique developments are coming on line to complement the new generation of synchrotron facilities.
6. Integrated multi-technique approaches are essential.

Summary: *Technical Challenges*



1. Increasing technology for generating extreme conditions:
→ *A new generation of devices*
2. Nanobeam capabilities and higher brightness at 10-20 keV
→ *In situ imaging at ever more extreme conditions*
3. Dynamics under extreme conditions
→ *Exploiting time domain (coherent sources)*
→ *Combined static/dynamic compression*
4. Integration with other techniques
→ *Magnetic and electric fields, photon fluxes, etc.*

